SESSION 6

KRYPTON, RADON, TRITIUM, CARBON-14 TREATMENT

TUESDAY: August 19, 1986
CO-CHAIRMEN: W. Motes
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FINAL RESULTS AND CONSEQUENCES OF THE DEVELOPMENT OF A CRYOGENIC KRYPTON SEPARATION SYSTEM
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OPENING COMMENTS OF SESSION CO-CHAIRMAN CROFF

This session is, in principle, concerned with the recovery, treatment, and disposal of relatively long-lived volatile radionuclides such as tritium, Kr-85, C-14, and I-129. The primary source of these radionuclides would be from nuclear fuel reprocessing plant effluents. They are important because their uncontrolled release has the potential to significantly increase the radiological impact of nuclear electricity generation.

It is apparently accepted that krypton, carbon, and iodine will have to be (or are being) recovered, treated to yield an acceptable waste form, and isolated using a technology appropriate to each radionuclide. The need to reduce releases of other radionuclides is still open to question, although recovery processes are currently being investigated. The subject of this session overlaps consideration of dissolver off-gas cleaning (Session 8), and it is there that some papers on iodine and tritium recovery will be given.

As I've noted, the need to investigate management of long-lived volatile radionuclides is closely related to the degree to which nuclear fuel will be reprocessed. The many worldwide delays in undertaking reprocessing have clearly resulted in greatly reduced work in the subject area of this session. Consideration of the likely near-term directions of reprocessing indicates that this situation is likely to persist for some time unless repository-related activities require the use of some of this technology.

FINAL RESULTS AND CONSEQUENCES OF THE DEVELOPMENT OF

A CRYOGENIC KRYPTON SEPARATION SYSTEM

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Abstract

After some ten years of development the test program carried out with the ADAMO and KRETA facilities for cryogenic separation of Krypton from the dissolver offgas of a reprocessing plant was brought to an end in a continuous campaign of three months of industry-like operation. The feasibility of the chosen concept has been demonstrated in some 20,000 hours of test operation.

The most important activity was the investigation, in cryogenic columns of the behavior of impurities within the offgas stream (O_2, CO_2, CH_4, NO_x) and of compounds which may form in the columns (O_3, N_2O_4) due to radiolysis.

Progress was made

- in effective removal of NO_x in the preparatory catalytic reduction step; NO_x can be removed from the process gas down to less than 1 ppm_v, which prevents plugging of the cryogenic column;

- in effective removal of ozone together with the xenon bottom product from the krypton-xenon separation column. Operating the column with continuous head and bottom product withdrawal, and suppressing pressure oscillations by careful control, allows the Xe-O_3 product to be kept free from krypton down to a few ppm_v.

Another topic of development was the reduction of the krypton inventory of the columns to reduce the activity inventory:

- While the principle of sieve plates was maintained, the column diameter was reduced and the design features of the plates were changed.

- Bottom product withdrawal of the first column was switched from the liquid to the gaseous from, which reduced the Kr concentration in the bottom liquid almost by a factor of 10.

- The most drastic activity reduction would result from replacing the sieve plate column by a packed colummn.

In three months of continuous operation no major malfunctions occurred. No long-term effects, such as dangerous accumulations or gradual plugging of parts of the installations, were observed.

Introduction

Ten years ago, in 1976, we built and commissioned the KRETA test facility, which has since been operated in 19 campaigns, each of them comprising several weeks of continuous operation, including a final long-term campaign of three months, to develop and test the low-temperature rectification technique for krypton removal from the dissolver offgas of a reprocessing plant (Fig. 1). This trial period corresponds to a cumulated period of operation of approximately 20,000 hours. In this way, we have proved the usefulness and reliability of the method, although we did not work with radioactive krypton in that phase.
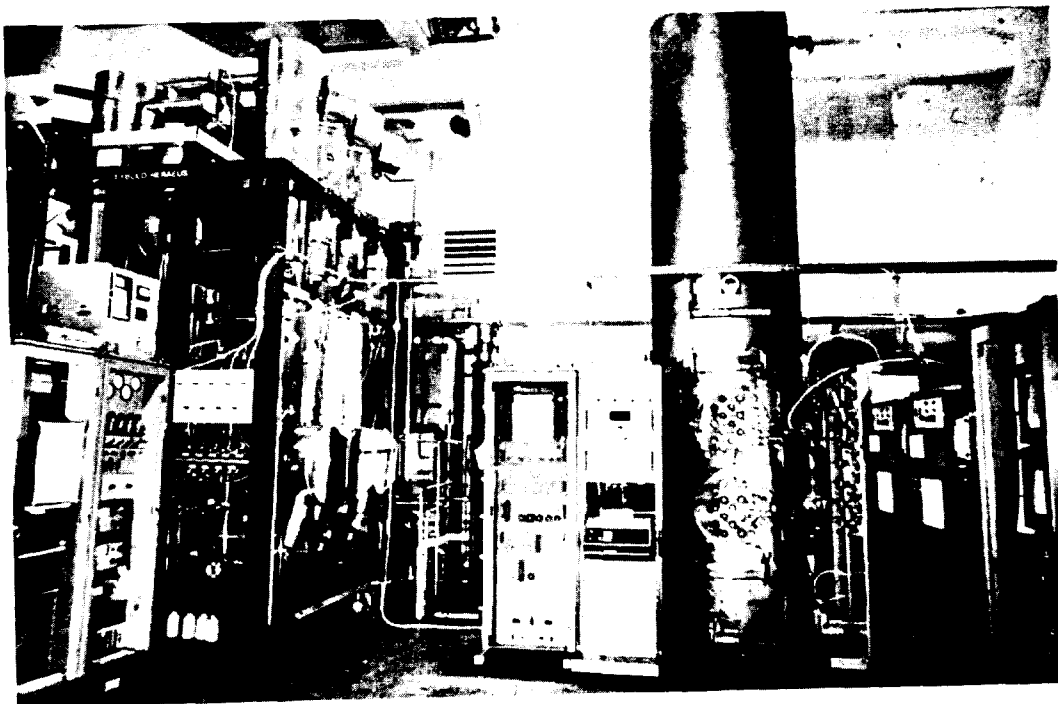
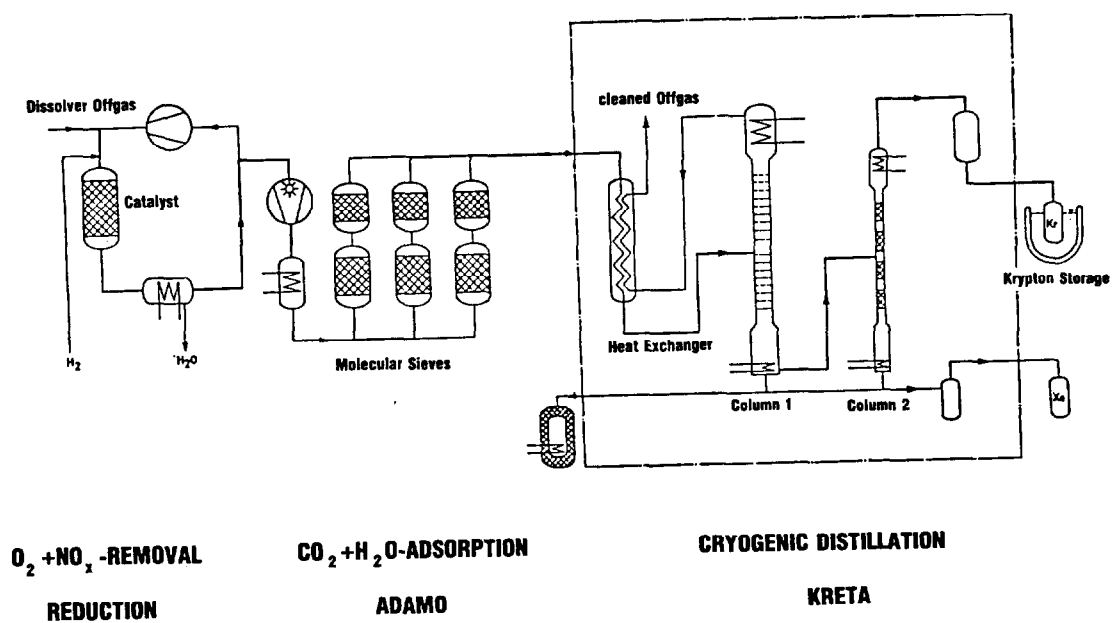**Fig.1: KRYPTON RETENTION FROM DISSOLVER OFFGAS**   **TESTFACILITIES ADAMO-KRETA**

O_2 +NO_x -REMOVAL CO_2+H_2O-ADSORPTION   CRYOGENIC DISTILLATION

REDUCTION   ADAMO   KRETA

Fig.2:   **KRYPTON RETENTION FROM DISSOLVER OFFGAS**
KfK TESTFACILITIES

The progress of our work has been reported at all Nuclear Air Cleaning Conferences since 1978 [1] [2] [3] [4].

The basic flowsheet of the process steps in cryogenic krypton removal (Fig. 2) as built up in Karlsruhe for a gas throughput of 50 m^3/h STP shows the preparatory removal of those impurities, which would freeze out at lower temperatures, in the following facilities:

- REDUKTION, for the catalytic reduction of oxygen and nitrogen oxides by means of hydrogen and removal of the water generated,

and, after a pressure increase to 5 bar by a water ring compressor,
- ADAMO, for the adsorptive retention of CO_2 and water in series connected silicagel and molecular sieve beds. Three such lines are arranged in parallel so that adsorption, flushing back of co-adsorbed krypton and xenon and regeneration can be carried out simultaneously in one operating cycle.

This is followed by the cryogenic section installed in a cold box (KRETA facility), consisting of the inlet heat exchanger, in which the gas is cooled to approx. 125 K, the first separation column (sieve plate column), in which the Kr and Xe noble gases are separated from the nitrogen carrier gas, and the second separation column (packed column), which separates krypton from xenon.

In addition, there is a dump tank to accept the liquid contained in the plant in cases of maloperation, and a filling device for noble gas.

Besides investigating the reliability of this process, our activities were concerned with the following main topics:

- Behavior of the highly volatile impurities (mainly O_2, CO_2, NO, and CH_4), which can still enter the cryogenic facility in ppm_v concentrations even after preparatory cleaning (Fig.3 and 4).
- Behavior of the ozone generated radiolytically out of oxygen, which we simulated by feeding ozone to the first separation column (Fig..3 and 4), and the movement of radiolytically generated NO_2/N_2O_4.
- The influence operating conditions exert on product composition.
- Determination of the decontamination factor of the whole facility.
- Accident studies (failures of column feed, heating and cooling) as well as equipment behavior in the presence of fluctuations in throughput and concentration.
- Development of cryogenic separation equipment so as to reduce the krypton inventory, i.e., the activity inventory.

Final Results

Let us now discuss the most recent findings and describe the latest process concept and equipment design.

Behavior of Nitrogen Oxides in the First Cryogenic Column

A distinction must be made between the NO_2 arising only in the first column as a result of radiolysis of N_2 or NO with O_2 [3] or of residual NO impurities carried into the column with O_2, and the NO_2 not retained in the preparatory cleaning step.
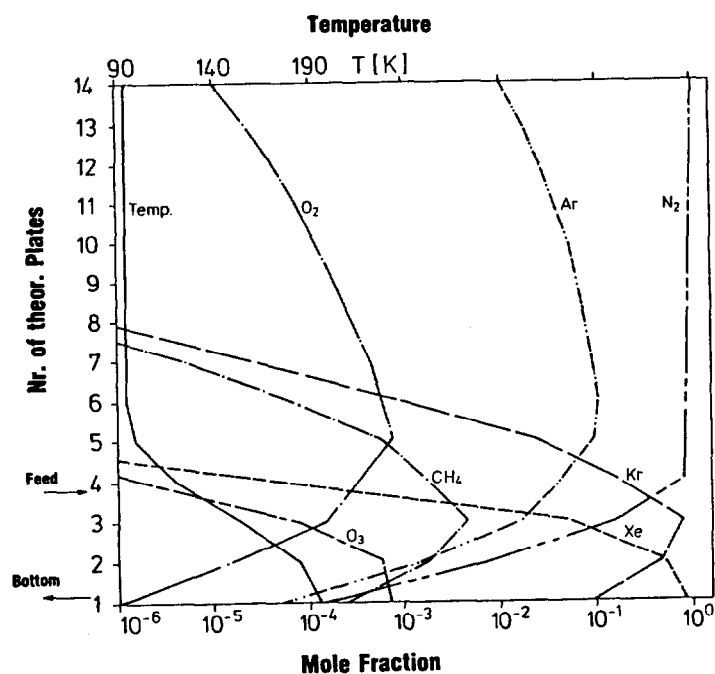
Temperature

Temp. O₂ Ar N₂

CH₄ Kr

O₃ Xe

Nr. of theor. Plates

Feed

Bottom

Mole Fraction

Feed:	50m³ STP/h
Reflux Ratio:	1
Pressure:	5 bar

Feedgas Concentration

Ar	1 vol%
Kr	400 vpm
Xe	4000 vpm
Ch₄	1 vpm
O₂	10 vpm
O₃	3 vpm
N₂	98.5586 vol%

calculated Data, Gas

Fig. 3: CONCENTRATION PROFILES IN THE FIRST KRETA COLUMN
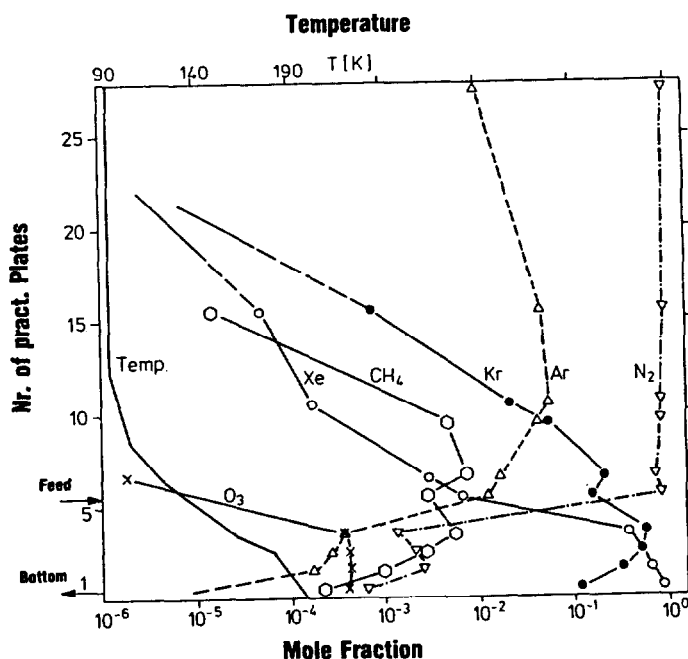
Temperature

Temp. Xe CH₄ Kr Ar N₂

O₃

Nr. of pract. Plates

Feed

Bottom

Mole Fraction

Feed :	50 m³ STP/h
Reflux Ratio:	~ 1
Pressure:	5 bar

Feedgas Concentration

Ar	1 vol%
Kr	400 vpm
Xe	4000 vpm
CH₄	1.2 vpm
O₃	3 vpm
N₂	98.55958 vol %

experimental Data, Gas

Fig.4: CONCENTRATION PROFILES IN THE FIRST KRETA COLUMN

In earlier experiments on the behavior of nitrogen oxides we were able to see that NO fed to the column indeed reacted with the oxygen present in the column at this low temperature to form NO_2 which, however, seems to dissolve in the liquid immediately and go to the column bottom. Only when the solubility limit in xenon of about 1 Mol% is exceeded it is precipitated there as a solid and thus does not upset column operation (aside from plugging up measurement lines, e.g., for measurement of the bottom level by means of the differential pressure, a situation which could be remedied by adopting a different measurement principle, such as capacitance level measurement) [3]. The same behavior is expected also of NO_2 generated by radiolysis.

However, when adding NO_2 as a residual impurity to the column feed we found that, at NO_2 concentrations above 1 ppm_v, the differential pressure across the first sieve plate gradually rises above the feed point and, over prolonged periods of operation, gradual plugging of the column must be expected. This results in the need to reduce in the preparatory cleaning step (catalytic reduction and adsorption) NO_x to levels of < 1 ppm_v. After we had begun to use a computer-supported hydrogen control system in the REDUCTION test facility we were able to meet this criterion even in process gas streams of varying compositions (Fig. 5). As NO is oxidized to NO_2 in the presence of O_2 on the molecular sieve even at room temperature, and the molecular sieve adsorbs NO_2, we also studied this retention possibility in a separate test series by means of ADAMO. We found that, at an O_2 concentration of at least 120 ppm_v, a residual NO concentration of 5 ppm_v was retained completely by our technical molecular sieve arrangement. In the presence of a lower O_2 excess, all NO was converted into NO_2, but NO_2 still broke through with >1 ppm_v.
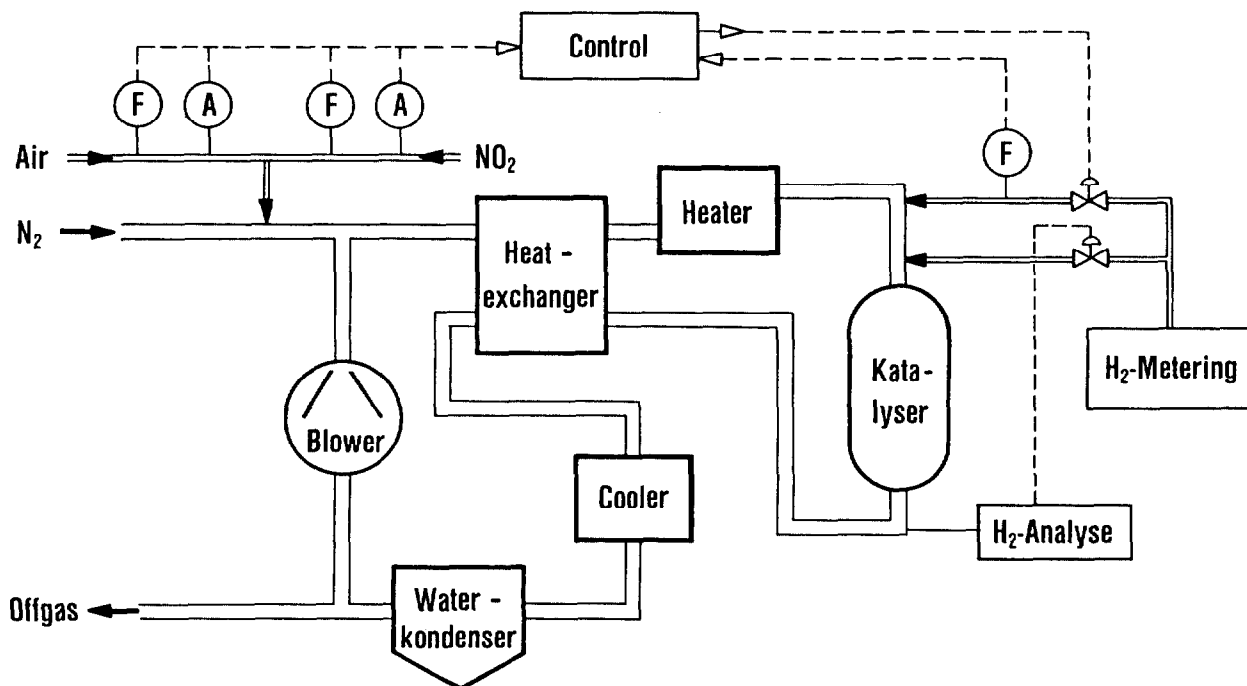
**Fig.5:** **H$_2$-METERING AT THE REDUCTION**

This aspect of making use of oxygen would be attractive if preparatory cleaning with selective NO_x reduction were applied, i.e., feeding O_2 to the separation facility. This would allow the criteria to be slackened which this NO_x retention would have to meet, for the adsorption unit would accommodate the residual nitrogen oxides.

In any case, however, in order to be on the safe side, we would arrange for two inlet heat exchangers and design them as regenerable cold traps, in case increased NO_x concentrations or also CO_2 and H_2O were to enter the cryo-facility as a result of maloperation or irregularities.

Purity of the Xenon Product of the Second Cryogenic Column

We were able to show that separating krypton from xenon in the second column is no problem if only these two substances are present or if highly volatile gases, such as N_2, Ar, O_2 or CH_4, get into this column in the mode of operation selected here, assuming, of course, continuous extraction of these gases at the top of the column. In this way, a xenon product can be achieved whose residual krypton fraction is in the ppb rang.

If one now traces the path of the ozone to be removed from the second column with the xenon bottom product, even a simulation calculation (Fig. 6) shows that the three component system of Kr, O_3,Xe is separated to the desired product purities in only a small number of theoretical stages. We put this separation part into the lower region of our column, the number of stages which is vastly overdimensioned anyway. This mode of operation minimizes the O_3 inventory and helps to keep the O_3 concentration far from the explosion limit of 8% ozone in xenon.
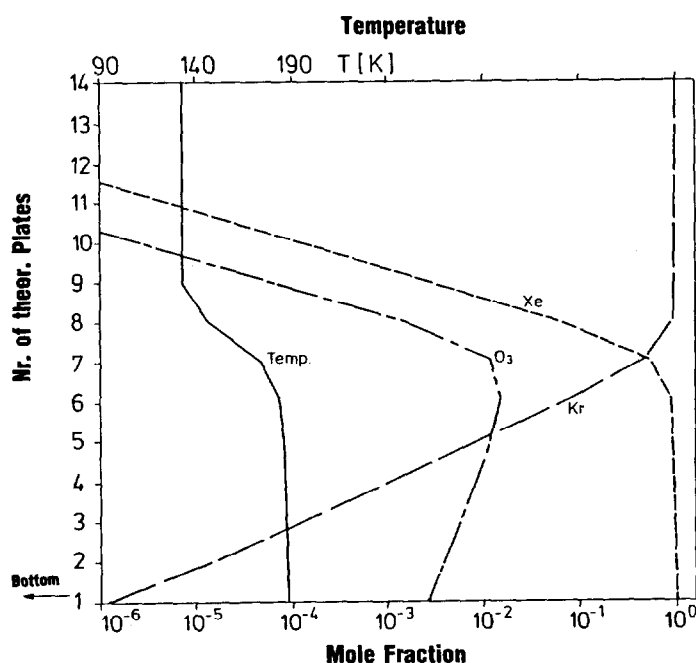
Feed:	176 l STP/h
Reflux Ratio:	150
Pressure:	3 bar

Feedgas concentration

Kr	9.083 vol%
O_3	0.068 vol%
Xe	90.849 vol%

HETP: 5 cm

calculated Data, Gas

Fig. 6:   CONCENTRATION PROFILES IN THE SECOND KRETA COLUMN

As far as technical control is concerned, this mode of column operation is easily achieved, but now the Kr front is so close to the xenon extraction that the residual krypton content in the xenon product may become worse as a result of minor fluctuations in the operating parameters. For example, our control concept included temperature control acting on the bottom heating system. Because of the steep slope of the temperature profile at this point, the transition from xenon to krypton, the set temperature was easily exceeded or underrun, the consequence being that bottom heating was controlled as in on-off control. This plus the batch extraction of the top product also resulted in minor pressure fluctuations which, in turn, affected the temperature. The result was a residual content of krypton in xenon of 40 to 400 ppm$_v$ in the continuous mode of operation. This means that this product can be released through the stack only after dilution which, at the same time, detracts from the decontamination factor of the whole plant.

However, the product would be quite suitable for commercial utilization of the xenon after a final cleaning procedure, e.g., by adsorption.

If the objective were to keep the residual Kr content in xenon very low in the continuous mode of operation, column control would have to be improved. The column pressure and the position of the separation interface between krypton and xenon must be maintained within very narrow limits. Control concepts serving this purpose are proposed in the literature [5]. We decided to do without such backfitting, but do not consider it to be a major problem.

Reduction of the Activity Inventory

One important objective of our work was the minimization of the krypton inventory, i.e., the activity inventory, in the plant. On the one hand, this was based on safety considerations and, on the other hand, less activity reduces the radiolytic formation of ozone and NO_2 [3].

We did two things in the first column:

(a) Maintaining the sieve plate principle, which we still consider to be most suitable for reasons of operational reliability, because of its low sensitivity to fluctuations in operation (throughput, concentrations and maloperation), we designed a new first column.

The modifications affecting the inventory were these:
- Reduction of the column diameter from 160 mm to 120 mm in the top part and 100 mm in the bottom part (with the reflux being increased from 0.58 to approx. 1.0).

- Reduction of the liquid content on the plates by changing the weir levels from 55 mm to 30 mm.

Design possibilities are limited by the area of the sieve holes needed for the gas flow. However, it was found that the area of the sieve holes as determined by the usual methods of computation can be underrun by a clear margin without entailing any drawbacks.

What is more important is a pronounced surge zone around the inlet and the outlet ducts to prevent flooding of the column. This was achieved by segmented weirs (Fig. 7).

(b) The activity inventory was further reduced by changing from the original extraction of the liquid of the noble gas-bottom product at the base of the bottom tank to gas extraction above the liquid level. In normal operation, the Kr/Xe ratio at the point of extraction is always established as a function of the

ratio of the feed concentration, i.e. 10/90%. In the case of liquid extraction, this is the composition of the bulk liquid in the bottom tank while, in the case of gas extraction, the liquid contains only some 1% of krypton.
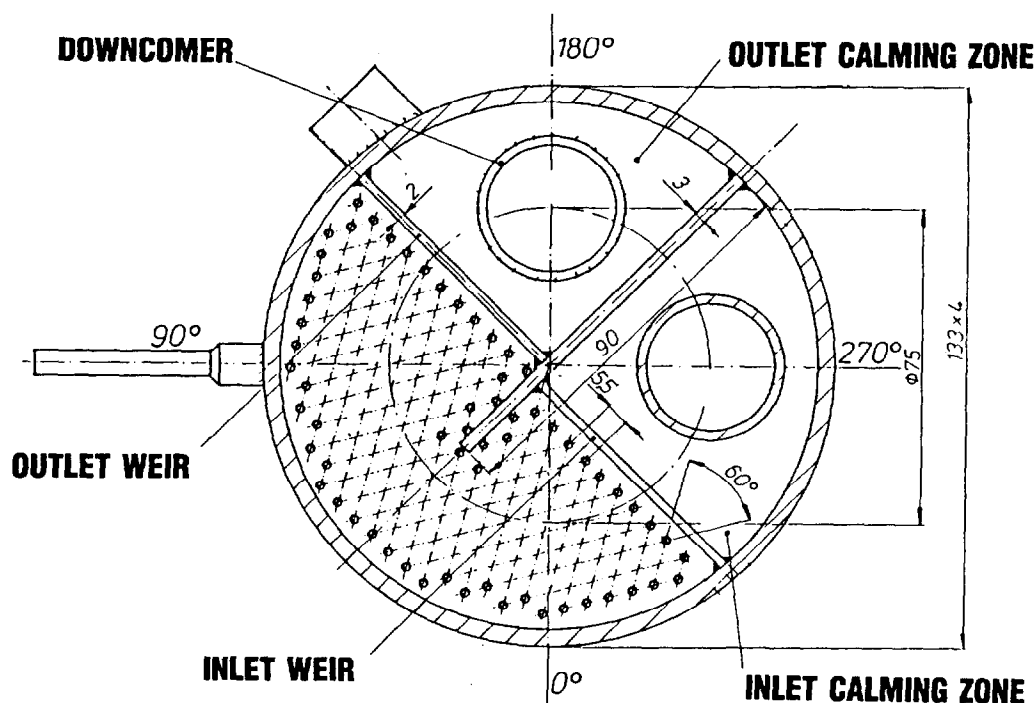
Fig. 7: IMPROVED SIEVE TRAY

Table 8 shows the activity levels of the old and the new KRETA columns designed for 50 m³/h STP. For extrapolation to 100 m³/h STP of offgas, wich would roughly be applicable to a reprocessing plant of 350 tons/a, this value would have to be multiplied by a factor of $\sqrt{2}$.

The most drastic activity reduction is brought about by the change from sieve plate columns to packed columns (Table 8). We decided not to take this step because our Belgian colleagues in Mol, in a similar, smaller facility, operated both separation units as packed columns and also achieved good results. In our second column we accumulated experience with packings.

In our opinion, packed columns are less stable to fluctuations in throughput and process gas composition; their reaction to disturbances is also less damped. Yet, if a low activity inventory in the plant is regarded as the more important factor (for safety reasons or because of the radiolysis products), we think the use of packings is feasible also in the first cryogenic separation column.

Table 8. Activity Inventory

FEED: 50m^3 STP/h

FEED COMPOSITION [vpm] :

N$_2$	Ar	O$_2$	CH$_4$	NO	Kr	O$_3$	Xe
98.56%	1%	10	1	1	400	—	4000

	KRETA first Design	KRETA new Design	KRETA package	
ACT.INV.	284300	120123	6060	Ci
COOLING	3293	3293	3293	Watt
HEATING	2378	2652	2743	Watt
	built	built	calcul.	

Total Inventory

Proposal of a Cryogenic Krypton Removal Facility

In conclusion of our work, our proposal for a cryogenic krypton removal plant for dissolver offgas is as follows (Fig. 9):

-   Catalytic reduction of oxygen and nitrogen oxides with the assistance of a computer-supported H$_2$ control system.

-   Pressure increase by means of a water ring compressor; a proven combination of materials in the slide bearings is special cast CrMo and Sb-impregnated hard carbon.

-   Adsorptive retention of CO$_2$ and water by the molecular sieve. Flushing and regeneration of the adsorber bed can be carried out simultaneously with adsorption in the parallel tank. This saves one line, or allows one line to be kept for standby purposes.

-   Zeolon 900H as an adsorber material proved to work just as satisfactorily as did the 10A molecular sieve, while the silicagel material tested is subject to accelerated aging in the presence of nitrogen oxide bearing offgas. For this case, a combination of Zeolon 900 H and a 10A molecular sieve is proposed.

-   The cryogenic part of the facility is installed in a vacuum insulation tank, which makes for good accessibility.

O$_2$ +NO$_x$ -REMOVAL   CO$_2$ +H$_2$O-ADSORPTION   CRYOGENIC DISTILLATION

REDUCTION   ADAMO   KRETA
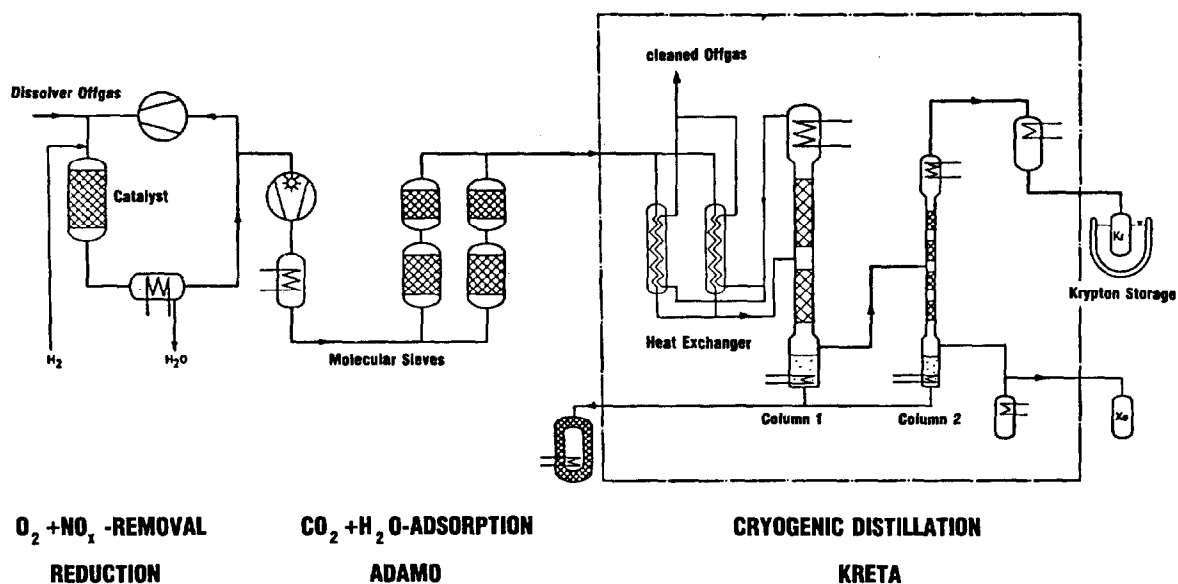
Fig. 9:   KRYPTON RETENTION FROM DISSOLVER OFFGAS PROPOSED FLOWSHEET FOR A PILOTFACILITY

-   For the inlet heat exchangers two parallel units are used, which are designed as a cold trap, can be switched and regenerated.

-   For reasons of activity minimization, the first separation column is a packed column.

-   The second column, also a packed column, is equipped with a sensitive control system for product extraction and pressure.

The next step now will have to be the construction of a pilot plant for active operation in conjunction with a reprocessing plant to allow radiological influences to be studied. This is being planned for the Wackersdorf facility; however, it is not yet certain which method of Kr removal will be employed.

References

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(3)   von Ammon R., Bumiller W., Hauss E., Hutter E., Neffe G., Hammer R.R., "Formation and behaviour of nitric oxides in a cryogenic krypton separation system and consequences of using air as process gas" Proceed. 17th DOE Nuclear Air Cleaning Conf. (First M.W.Ed.), CONF-820833, p. 683, 1983

(4)   von Ammon R. Bumiller W., Hutter E., Knittel G., Mas C., Neffe G.,
       "Behaviour of impurities in a cryogenic krypton removal system"
       Proceed. 18th DOE Nuclear Airborn Waste Management and Air Cleaning Conf.
       (First M.W.Ed.), CONF-840806, p.951, 1985

(5)   Ullmanns Enzyklopädie der Technischen Chemie, Vol. 2, 1972, p. 535.

KRYPTON RECOVERY BY CRYOGENIC DISTILLATION
WITHOUT PRECEDING OXYGEN ELIMINATION

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Abstract

By applying the proper operation mode for cyrogenic distillation, ozone accumulation can be reduced or even be prevented to the extent that oxygen might be allowed in the feed gas of a cryogenic krypton recovery unit in future installations.

The behaviour of oxygen and ozone in the S.C.K./C.E.N. cryogenic distillation unit was investigated. The presence of oxygen resulted in new temperature and concentration profiles in the first rectification column, without affecting the operation of this column. No oxygen was detected in the liquid krypton-xenon bottom product, so that no oxygen was transferred to the second batch distillation column. Ozone accumulated in the krypton-xenon mixture. Its decay was measured in absence and in presence of a thulium-170 radiation source. The higher decay rate, observed with the radiation source, indicates that ozone accumulation might be prevented by providing the proper radiation intensity in the kettle of the rectification column.

The feasibility of cryogenic distillation for krypton removal from an air carrier stream was demonstrated with an inventory of 4.44 TBq krypton-85, during a 900 hours campaign.

I. Introduction

Two operation modes are possible for the cryogenic recovery of krypton, depending on the absence or presence of oxygen in the feed gas of the cryodistillation unit. In the past, absence of oxygen was preferred in order to avoid the accumulation of ozone, which represents a serious explosion risk. Ozone was indeed observed to accumulate in the rectification column of the ICPP krypton recovery plant, which was fed with air ([1], [2], [3]). However, the removal of oxygen creates a similar safety problem by the use of a catalytic oxygen reduction process with hydrogen. Moreover, this process substantially increases the costs of an integrated off-gas cleaning system.

Presently, the second operation mode, allowing oxygen in the feed gas of the cyrogenic distillation unit, is more favoured. Laboratory experiments were carried out to investigate the formation and the destruction of ozone in a β-γ radiation field. These experiments revealed that the G-values for ozone destruction were much higher than for ozone formation, in both gaseous and liquid krypton-xenon mixtures ([5]). This information, combined with the operational control for a cryodistillation unit as developed at the S.C.K./C.E.N., indicates that the accumulation of ozone in the rectification column can be reduced to a great extent ([4], [6]). In this framework, the behaviour of both oxygen and ozone in the S.C.K./C.E.N. cryodistillation unit was studied. Particularly the ozone decay rate in the krypton-xenon bottom product of the rectification column has been measured. The influence of a radiation source on the decay rate was investigated. Finally, the feasibility of cryogenic krypton recovery from an air stream was demonstrated with radioactive krypton-85, during a campaign of limited duration.

II. The S.C.K./C.E.N. cryodistillation unit

Figure 1 shows a flow sheet of the cryogenic distillation unit, as it was developed at the S.C.K./C.E.N. in Mol. The unit essentially consists of two parallel heat exchangers, a first packed rectification column and a second packed batch distillation column, mounted in a insulated cold box.

The feed gas is cooled in the heat exchangers by the exhaust stream and by the vapours of the liquid nitrogen fed to the condensors of the distillation columns. Krypton and xenon are separated continuously from the feed gas in the first rectification column. The liquid krypton-xenon mixture is transferred from the first to the second distillation column, where both noble gases are separated from each other by batch distillation.

A more elaborate description of the unit and its operation mode has already been given earlier ([4]). Table 1 summarizes the main operational characteristics of the principal part, the rectification column.

Table 1 : Characteristics of the rectification column

Gas flow rate	:	$25 \ Nm^3 .h^{-1}$
Operating pressure	:	0.70 MPa
Inlet temperature	:	124 - 134 K
Reflux ratio	:	0.3 - 1.0
Packing material	:	3 x 3 x 0.4 mm S.S. springs
Upper packing	:	h = 0.80 m, d = 0.10 m
Lower packing	:	h = 0.72 m, d = 0.07 m

III. Oxygen behaviour in the cryodistillation unit

Three different oxygen concentrations were fed to the cryodistillation unit : 6, 12 and 21 vol. %. This resulted in new temperature and concentration profiles in the rectification column, without affecting the operation of the column itself. Those profiles were already reported and commented in earlier publications ([7]).

In Table 2 the oxygen concentrations, measured in the gas phase, at the different sampling points of the first column are summarized. The oxygen concentration measured in the krypton-xenon bottom product was less thant 0.1 vpm, the detection limit of the oxygen monitor used. This means that no oxygen will be transferred to the second batch distillation colun, if also ozone accumulation can be avoided in this bottom product. The differences observed between the feed gas and the outlet gas concentrations were within the accuracy of the analytical method used.

Table 2 : Oxygen concentrations in the first column

Experiment number	Feed vol. %	Out vol. %	AP 2 vol. %	AP 7 vpm	Bottom vpm
1	6.0	6.2	7.0	< 0.1	< 0.1
2	12.0	12.1	13.0	< 0.1	< 0.1
3	20.9	20.9	22.8	< 0.1	< 0.1

Note : AP 2 = in the feed zone of the column
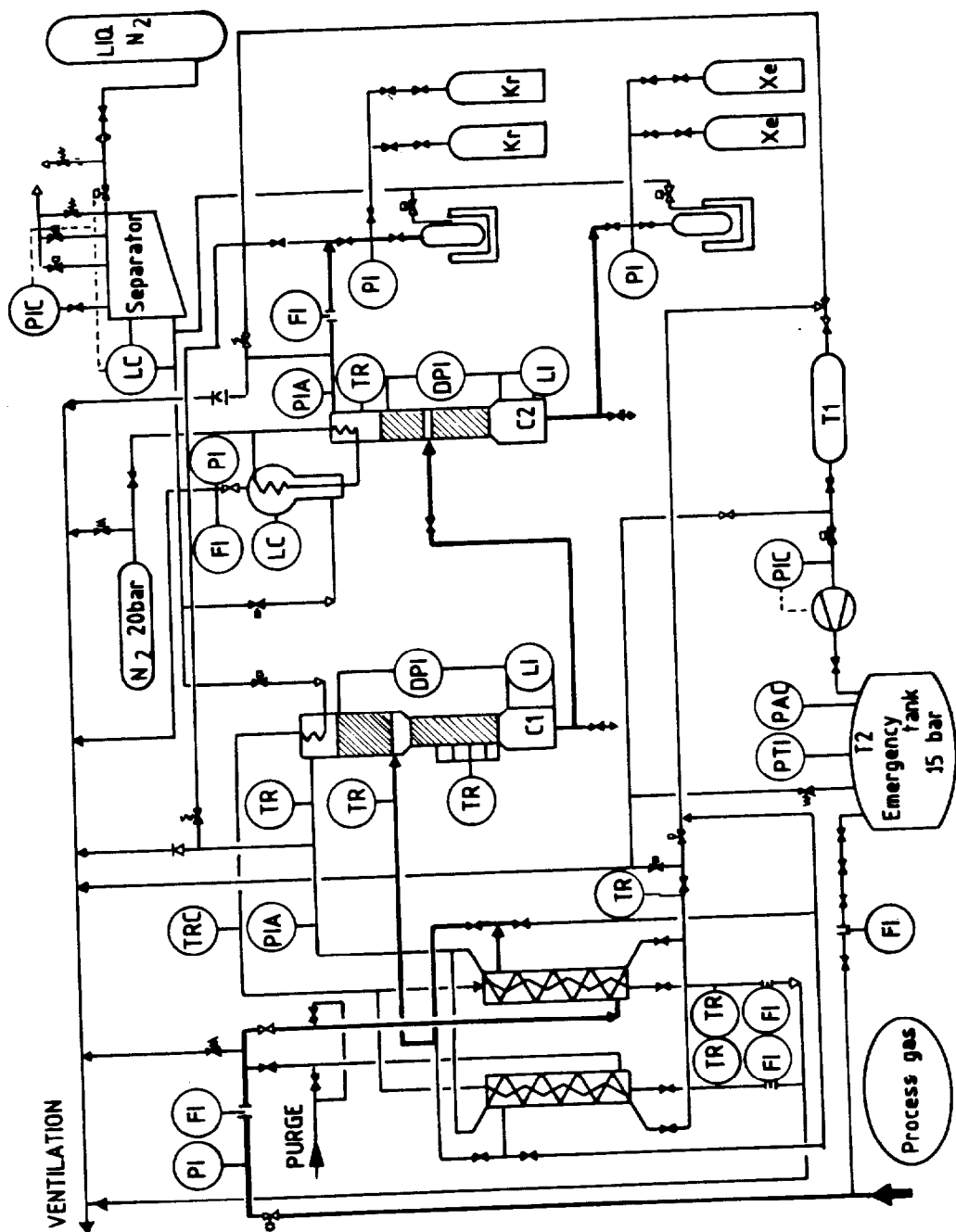AP 7 = in the pure krypton zone, in the lower packing

Fig. 1 : Cryogenic distillation unit

IV. Ozone behaviour in the rectification column

Ozone was fed to the rectification column at concentrations from 30 to 140 vpm, in an air carrier stream. No ozone was detected in the upper packing, nor in the outlet gas stream. All the ozone was found to accumulate in the liquid bottom product. For safety reasons, the accumulation was limited to about 1 vol. %. Table 3 summarizes the results of the ozone analyses at the different sampling points.

Table 3 : Ozone concentrations in the first column

Experiment number	Feed vpm	AP 4 vpm	Out vpm	Bottom
1	35	< 0.4	< 0.4	acc.
2	90	< 0.4	< 0.4	acc.
3	140	< 0.4	< 0.4	acc.

Note : AP 4 = in the upper packing
acc. = accumulation

Since ozone was accumulated in the krypton-xenon bottom liquid of the first column, its chemical behaviour there was investigated in greater detail. Particularly, to study the influence of the radiation field, the ozone decay rate was measured in absence and in presence of a thulium-170 source, which was installed in the kettle of the rectification column. Additionally, a short campaign was run to gain some information on the formation of ozone.

The use of the ^{170}Tm source for studying the influence of radiation on the ozone decay rate resulted from a survey of potential radiation sources. Taking into account the local implantation and shielding of the cryodistillation unit, a γ-emitter was excluded. For radioprotection reasons a β-emitter with limited γ- and bremsstrahlung was recommended, and on the basis of decay energy, half-life and availability considerations a thulium-170 source was chosen. The ^{170}Tm was obtained by irradation of the monoisotopic natural thulium metal (^{169}Tm, 100 %) in the BR2 reactor. By decay, the β-emitter ^{170}Tm is transformed to the stable ytterbium-170 isotope. The β-decay energies of ^{170}Tm are somewhat higher than those of ^{85}Kr : 23 % of 0.89 MeV and 77 % of 0.97 MeV, rather than 100 % of 0.67 MeV. On the other hand, for practical reasons the 129 days half-life of ^{170}Tm, is very well suited for the relatively short experiment which was planned to last 1000 hours. Besides its radiation properties, thulium metal has the advantage that it is chemically stable in the medium where it was to be used.

In Figure 2 the decay curves for ozone in the liquid bottom product are given, with and without the radiation source. Without the thulium-170 source, it took almost 30 days to observe a decay from 0.90 to 0.45 vol. %. The decay rate slightly decreased with decreasing ozone concentration. In the presence of a 18.5 TBq thulium-170 source an almost constant decay rate was observed, which resulted in a complete decay from about 1.05 vol. % to zero in 4 days. After two half life periods of the thulium-170, i.e. with a 4.63 TBq source, also a constant decay rate of about 0.20 vol. % per day was observed during the first days. Later on, the decay rate decreased with decreasing ozone concentration, which resulted in a complete decay from 1.05 to 0 vol. % in about 10 days.

The qualitative conclusion which can be drawn from these experiments, is that the possibility exists to prevent ozone accumulation in the bottom liquid of a cryodistillation column by providing the proper radiation intensity. However,
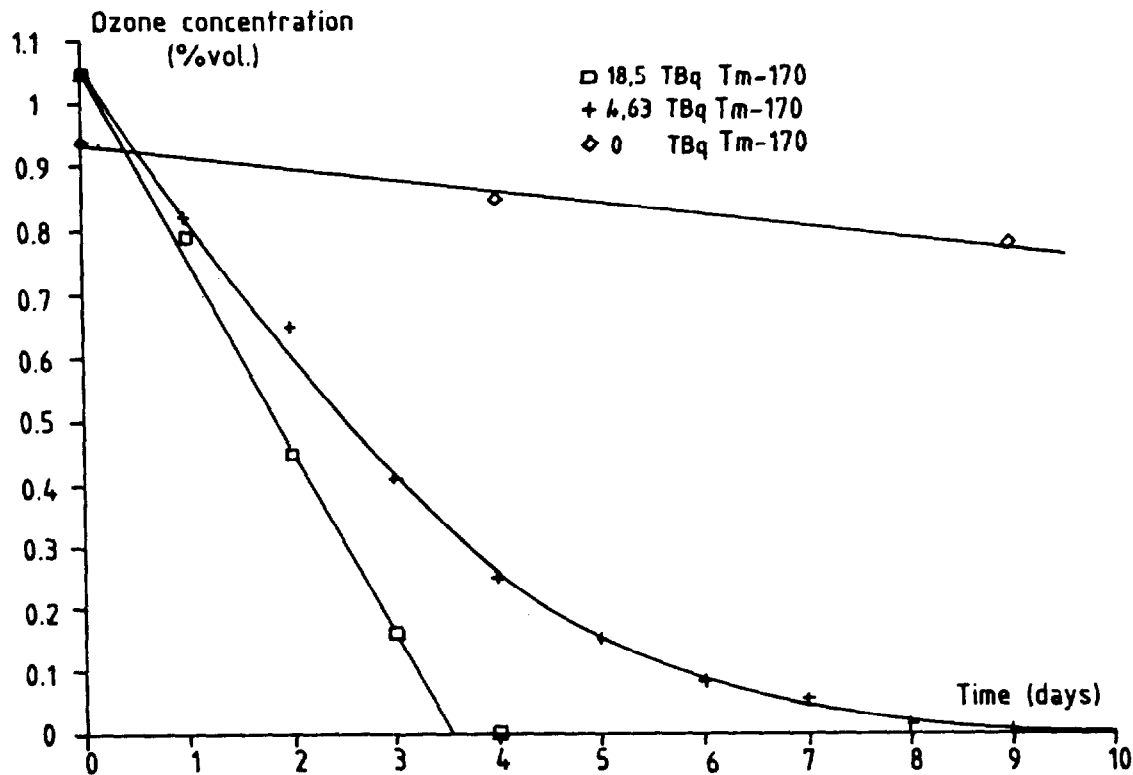
Fig. 2 : Ozone decay:influence of radiation

quantitative interpretation of these data is difficult. Indeed, there are too many unknown parameters, which influence the decay rate :
- the presence of radioactive by-products,
- the degree of dispersion of the ^{170}Tm source.

In addition to the ozone decay characteristics, also the ozone formation was investigated. In particular non standard operating conditions of the unit, oxygen was accumulated in the noble gas mixture in the kettle of the rectification column, up to 12 vol. % in presence of the 18.5 TBq thulium source. Even at this relatively high oxygen concentration, no ozone was detected after a period of 18 hours. This experiment was limited in time, since under the prevailing operating conditions, proper control of the column is very difficult.

V. Cryogenic distillation in presence of krypton-85

As the final step of the experimental programme the feasibility of cryogenic distillation in presence of oxygen was demonstrated under moderate radioactive condition, using 4.44 TBq krypton-85. For this purpose, both columns and all krypton and xenon containing bottles of the installation were shielded with 2 cm of lead. A 6 cm lead shielding as provided, for the kettle of the rectification column, which also contained the 18.5 TBq ^{170}Tm source.

In the experiment, radioactive krypton-85 was fed to the cryodistillation unit in an air carrier stream, at about 1.11 GBq.h^{-1}. The maximum inventory of

^{85}Kr in the rectification column amounted to 1.5-1.8 TBq. The campaign lasted for almost 900 hours, and no special problems due to the presence of the radioisotope were encountered. The only problems that occurred with the ^{85}Kr, concerned the transfer of the rather concentrated ^{85}Kr from the delivery containers into the storage bottles of the cryodistillation unit.

VI. Conclusions

The experiments with oxygen in the feed stream of the cryogenic distillation unit revealed that the operation of the unit was not influenced by the presence of oxygen, not even at concentrations corresponding to an air feed stream. Furthermore, in the liquid bottom product of the recification column no oxygen has been detected.

On the other hand, ozone was found to accumulate in the bottom liquid, Nevertheless, when its concentration was limited below 1 % volume, no operational problems occurred. After accumulation up to 1 % volume, its decay was measured in the absence and in the presence of a ^{170}Tm source. The conclusion of these experiments was that ozone accumulation can be prevented by providing the proper radiation intensity in the kettle of the rectification column. The observation of the oxygen and the ozone behaviour allows to conclude that no oxygen, neither as molecular oxygen, nor as ozone, will be transferred to the batch distillation column in this case.

Finally, the feasibility of cryodistillation for krypton recovery is presence of oxygen was demonstrated with 4.44 TBq krypton-85, during a 900 hours campaign.

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Acknowledgement

PILOT PLANT DEVELOPMENT FOR ADSORPTIVE KRYPTON SEPARATION
FROM DISSOLVER OFF-GAS

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Abstract

In view of hot cell application a separation process was investigated for the retention of Kr-85 from gaseous effluents. In the flow sheet only adsorption beds are applied. The most efficient process scheme is adsorption of the noble gas on activated charcoal and thereafter separation of the coadsorbed gas species like N_2, O_2, Xe and CO_2 from the krypton by gas chromatography. Adsorption is at normal pressure and low temperatures of up to -160°C, whereas desorption is at elevated temperatures and under helium purge. Influences on the process operation like off-gas composition, adsorption temperatures and adsorbent are experimentally investigated, as well as the behaviour of trace impurities in the adsorption columns. On the basis of pilot plant operation the main components for a full scale facility are being designed.

I. Introduction

In recent years at KFA Jülich a new process has been developed for the separation of radioactive noble gases from the gaseous effluents of nuclear installations. A specific goal is the retention of Kr-85 from the dissolver off-gas of a reprocessing facility, such as the planned German reprocessing plant at Wackersdorf. The entire flow sheet of this Kr-85 retention process is based on adsorption/ desorption principles only and should therefore result in a simple and reliable process for hot cell application.

II. Process Principles

In a number of different laboratory experiments for adsorptive Kr separation from air, including: pressure swing, temperature swing and gas chromatography, a specific process scheme was selected (1,2). The main principles of the selected process are adsorption of krypton and xenon on activated charcoal at very low temperatures and regeneration of the adsorption beds by temperature rise and helium purge. Figure 1 shows the process principles. One process line consists of two adsorption columns of indentical design filled with chromatography-grade activated charcoal. During adsorption the first column is cooled to -130°C and the second one is cooled as low as -160°C.

COLUMN AT END OF ADSORPTION SEQUENCE:

COL.1: -130°C   COL.2: -160°C

OFF-GAS   Xe-MTZ   Kr-MTZ   CLEANED OFF-GAS

COADSORBED AIR
(3% OF OFF-GAS)

COLUMN DURING CHROMATOGRAPHIC Xe,Kr SEPARATION:

AIR/He
(Xe/He)

COL.1: -30°C   COL.2: -60°C

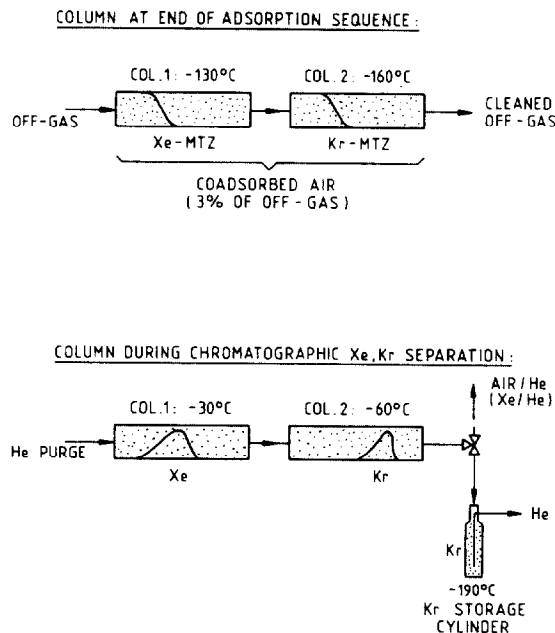He PURGE   Xe   Kr

He

Kr

-190°C
Kr STORAGE
CYLINDER

Figure 1: Process principle for adsorptive/chromatographic krypton
         separation process

Under these conditions Xe will adsorb completely in column 1 and the
Kr will adsorb partly in column 1 and partly in column 2. At the
end phase of the adsorption sequence the following gas distribution
will be approximately present in the two columns:

The xenon is adsorbed in the first third of column 1 whereas about one
half of the krypton is adsorbed across in column 1 and the other half
part is adsorbed in the first third of column 2. Together with the
noble gases, air is co-adsorbed across both columns and namely about
3 % of the full amount of the off-gas air will be adsorbed, i.e. 97 %
of the off-gas was cleaned during the adsorption sequence and left
the columns.

For column regeneration and final separation of the krypton from the
co-adsorbed air, both columns are heated up in a specific manner,
while being purged with a small amount of helium. These regeneration
parameters are selected in such a way that a pure Kr/He mixture can
be collected at the column exit.

Final Kr/He separation is done directly in the krypton storage
cylinder. Therefore this storage cylinder is filled with activated
charcoal as well and has to be cooled in the lower part with LN_2
for the filling operation. While the Kr/He gas mixture is fed into
the top of the storage cylinder, the krypton is completely adsorbed
on the charcoal and pure helium leaves the storage cylinder from the
cylinder bottom by means of a lower exit pipe.

III. Laboratory Experiments

The results of laboratory experiments are reported in detail in ref.
(2) and therefore they will only be summarized here. For the experi-

ments adsorption columns as shown in Fig. 2 were used. The columns had an adsorption bed of 35 mm diameter and 500 mm length, filled with activated charcoal of .50 to .85 mm grain size. Two such columns form one separation unit. The pressure drops for both columns (including two heat exchangers) at adsorption temperature of -130°C and -160°C respectively and a typical gas flow of 1 m³/h STP was .2 bar.

The parameters for a typical experiment were as follows:

- gas batch for one separation cycle: 2 m³ STP
- gas composition: dry air with .01 vol% Kr and .10 vol% Xe
- adsorption time: 2 h
- gas flow during adsorption: 1 m³/h STP
- temperature of column 1: -130°C
- temperature of column 2: -160°C
- pressure at column entrance: 1.2 bar
- pressure at column exit: 1.0 bar
- time for column regeneration (including subsequent time for column cooling): 2 h
- helium comsumption for regeneration: 4 % of gas batch
- decontamination factor for Kr: $\geq$ 1000
- concentration of separated Kr: $\leq$ 99 %
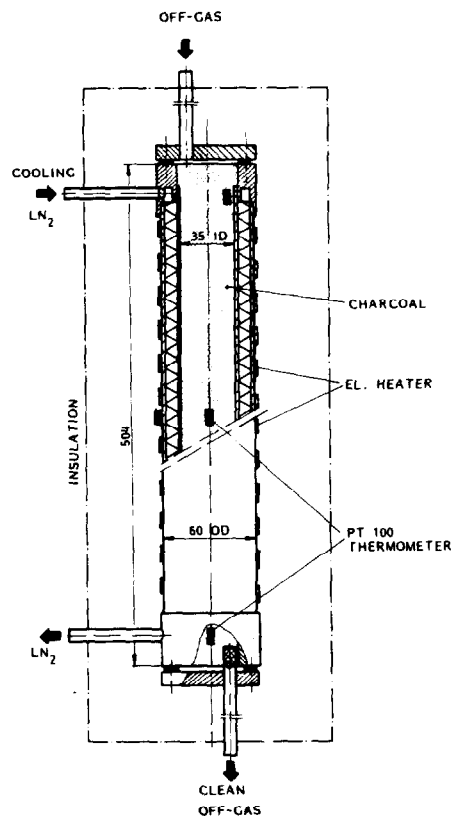
Figure 2: Kr separation column for laboratory experiments

The influences of the following operation parameters were investigated:

Off-Gas Composition

An increase of the typical noble gas concentration by a factor of 2 or 3 hardly influenced the separation results. Whereas a considerable noble gas increase to e.g. .2 vol% Kr and 2 vol% Xe does reduce the off-gas batch which can be cleaned in one process cycle.
Temporary high fluctuations of the noble gas concentration in the off-gas did not influence process operation; all these fluctuations will be levelled out in the adsorption columns during the adsorption sequence.

Adsorption Temperatures

In principle, the separation capacity increases e-functionally with decreasing adsorption temperatures; so the above mentioned column temperatures are the lowest temperatures possible for the following reasons:

For 1st column the lower temperature limit is about -130°C, because below that temperature xenon will freeze out. Even if plugging is avoided, the separation of Kr and N_2 from Xe is considerably impaired if the adsorption temperature is below -130°C because the xenon is too greatly polluted by Kr and N_2.

For the 2nd column the limit is about -160°C if 20 vol% O_2 is in the off-gas. Below -160°C this O_2 will condense in the charcoal micropores, so that the adsorption capacity of the charcoal for Kr is reduced. For off-gas without O_2 the temperature could be decreased as low as -180°C.

Behaviour of Trace Impurities

In the precleaned off-gas are - besides krypton and xenon - further gas species with small concentrations. The behaviour of the following gases in an adsorptive separation process was investigated:

- N_2O from dissolution process
- CO_2 mainly (300 ppm) from the dissolver purge air (containing some C-14)
- argon (about 1 vol% in air)
- CH_4 (ppm traces in air)

The operation diagram Figure 3 shows the behaviour of these gases in the experimental facility for one operation cycle. In order to achieve a distinct separation of all gas species only 1 m^3 STP off-gas was cleaned and a relatively small temperature increase, i.e. a long-lasting column regeneration programme, was chosen.

Argon behaves like N_2 and O_2, and is therefore not separated from the basic air species; N_2 and O_2 are also hardly separated from each other on charcoal. N_2O and CO_2 behave very similarly and therefore could only be separated from each other with an even longer temperature rise programme.
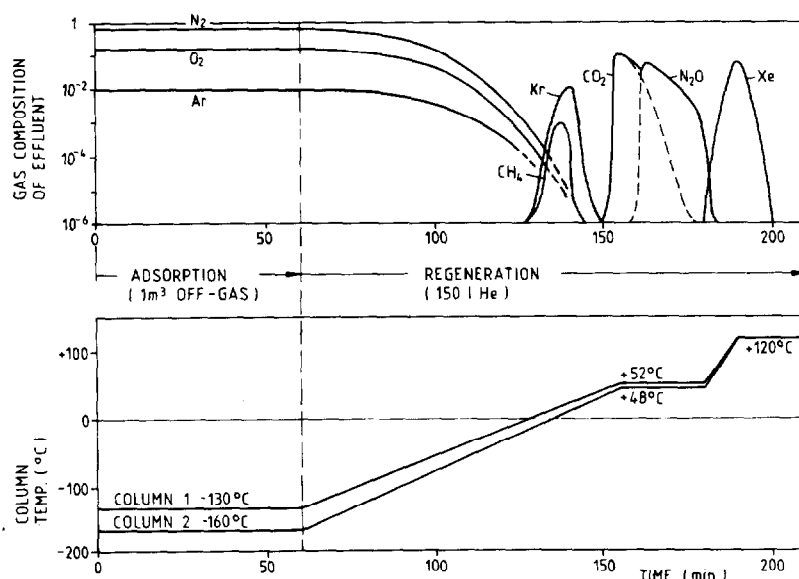
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Figure 3: Behaviour of trace impurities in the activated charcoal columns during Kr separation process (dry air with 1000 ppm Xe, 1000 ppm N_2O, 100 ppm Kr, 10 ppm CH_4)

At normal process operation Xe, N_2 and CO_2 will not be separated from each other, i.e. these gases will be collected in one batch. They could be separated from each other by a different gas separation process if desirable. The methane trace is not separated from krypton, i.e. it will be flushed from the column at each operation cycle and therefore does not represent a safety risk.

Selection of Adsorbent

The typical adsorbent throughout the experiments was a gas chromatography grade activated charcoal with the following specifications:
- grain diameter: .5 to .85 mm
- poured density: 440 g/l
- specific surface: 1050 m^3/g

This charcoal was most efficient for chromatographic gas separation. But due to its relatively small grain size the pressure drop during adsorption is high, so that for technical application a charcoal with larger particles might be more economical.

Apart from this, for safety considerations in hot cell application one would consider applying a ceramic adsorbent instead of activated charcoal. The experimental investigation showed that for large-scale Kr/N_2 separation charcoal can hardly be replaced by molecular sieve. In contrast to that, for preseparation of Xe 5A molecular sieve could be used. This would result in a process flow sheet with one enlarged molecular sieve and one charcoal column.

Ag exchanged molecular sieve showed a very poor adsorption capacity for Kr and is therefore not practical.

IV. Pilot Plant Experiments

For full-scale plant developments adsorptive off-gas cleaning will be experimentally tested for an off-gas flow of up to 10 m^3/h STP, and both for NO_x, H_2O separation as well as for Kr, Xe separation.

NO_x, H_2O Separation

After precleaning, (NO_x wash column, aerosol and iodine filtration) the dissolver off-gas will still contain, besides the noble gases, NO_x and H_2O residues in the order of .5 vol% NO_x and 2 vol% H_2O. This water will also be contaminated with some tritium, as HTO.

For the separation of these species the adsorptive retention on molecular sieve was investigated on a laboratory scale (3).

Applying the selected acid resistance molecular sieve an appropriate process was tested on a 1 m^3/h STP off-gas scale. The flowsheet consisted mainly of two adsorption columns in parallel arrangement so that the simulated off-gas could be cleaned continuously. The main test parameters were as follows:

- column dimensions: 64 mm ID., 430 mm length
- molecular sieve: "900 H Norten", SiO_2/Al_2O_3 = 10/1, 8-9 Å,
  1.8 mm DIA. extrudates
- gas flow: 970 l/h STP
- gas composition: wet air with .51 vol% NO_x and .5 vol% H_2O
- time for 1 ppm NO_2 breakthrough: 10.7 h
- time for breakthrough of 1/2 NO_2 inlet concentration: 14.2 h

From these data, one can calculate the length of the MTZ as 210 mm and the dynamic loading as 47 l STP NO_2/l molecular sieve.

The experiments showed that NO_2 would always break through before NO breakthrough occurred, which is a strong indication that in the column all NO of the gas will be oxidized to NO_2 and afterwards adsorbed.

Regeneration of the molecular sieve was accomplished by heating to 250°C and flushing the column with a small amount of air. For up to 50 adsorption/desorption cycles the adsorption characteristics of the molecular sieve did not change.

Kr and Xe Separation from Off-Gas

The final krypton/air separation is accomplished by gas chromatography. For this process sequence the separation column is purged with helium and heated up in a certain way. Since only a very small helium flow is needed, the column has to be heated by heat conductivity from the column outside. In order to have an undisturbed gas separation process during this heat-up it is most important to achieve a relatively small temperature gradient perpendicular to the gas flow, i.e. in the cross section of the column. The poor heat conductivity of activated charcoal cannot fulfil this process demand.

Therefore, for the process scale-up a different column design was chosen with respect to the laboratory-scale column. A cross section of this pilot plant column is given in Figure 4. In principle the charcoal bed is shaped like an annulus, with an annulus thickness of 17.5 mm. The inner and outer wall of the annulus can be cooled by a cooling medium and heated by an electric resistance heater, which is integrated into both walls. With the dimension of the charcoal bed being OD = 60 mm, ID = 25 mm, and length = 615 mm one separation column would contain 1.45 l charcoal.

With two of these columns in series an off-gas flow of 3 m^3/h STP containing air with .1 vol% Xe and .01 vol% Kr could be processed. The result of a gas separation experiment is shown by the operation diagram in Figure 5.
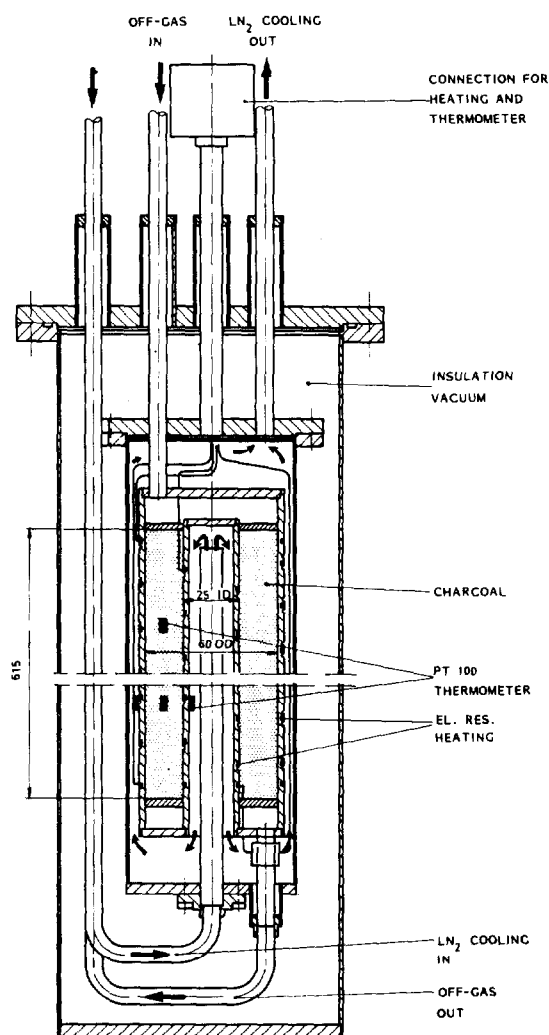
Figure 4: Kr separation column for pilot plant
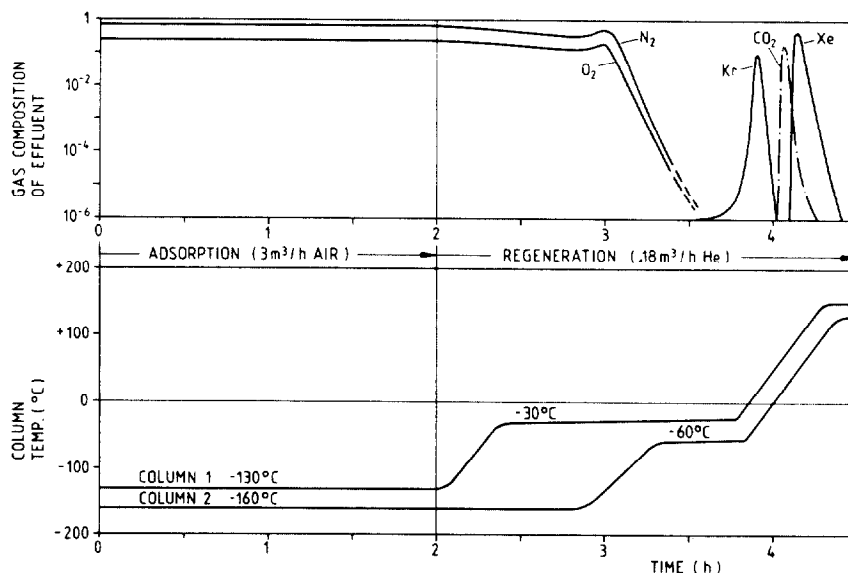
Figure 5: Operation diagram for cleaning 6 m³ STP off-gas in pilot plant (2 columns with 1.45 l activated charcoal each)

During the adsorption sequence of two hours 6 m³ STP of off-gas flowed through the columns. Pressure at the column entrance was 1.2 bar, the off-gas temperatures were -130°C and -160°C, respectively. During column regeneration and gas chromatography sequence the helium flow was 3 l/min STP, so that for 2.5 h regeneration time 450 l He was used. The separated Kr batch contained about 1 vol% N_2, the Kr decontamination factor was determined as about 1000. The accuracy of these two values is determined by the accuracy of the quadrupole mass spectrometer which was applied for gas analysis. For Kr the detection limit was about 1 ppm and for air (N_2, O_2) some 100 ppm.

Subpressure Operation

For hot cell operation, it is typically favourable if a process operates at a pressure below atmospheric. Therefore adsorptive Kr separation was also tested under subpressure conditions.

In this case, the off-gas was sucked through the two-column arrangement by a vacuum pump at the exit of the second column. For 3 m³/h STP off-gas flow and process temperatures in the columns, pressure at the column exit was .6 bar if pressure at the column entrance was 1.0 bar, i.e. the pressure difference was doubled with respect to operation at normal pressure at the column exit.

The results for the gas separation was in principle similar for both cases, i.e. identical gas batches could be processed. A main difference was noted for the second part of the chromatography sequence. About 10 min before full Kr breakthrough some Kr (up to 100 ppm) would elude from the column together with the N_2/He effluent. In order to reduce or to avoid this Kr leakage the heating rate during column regeneration has to be reduced, which results in a longer regeneration time or a few litres of Kr-contaminated effluent have to be recycled.

Apart from the column for 3 m^3/h STP gas flow, columns for 10 m^3/h STP with an identical design principle to that shown in Figure 4 have been constructed. Testing of these columns has yet to be done.

V. Engineering Design for Full-Scale Plant

Adsorptive Kr-85 separation from dissolver off-gas is a batchwise process as well as fuel dissolving itself. Therefore it might be favourable to adapt the sequence of this Kr-85 separation process to the sequence of the dissolution process. The main point is that only fuel element chopping and primer dessolution are the principle process steps when Kr-85 is liberated into the dissolver off-gas. During the other dissolution process steps, like: - secondary dissolution, iodine stripping, dissolver cooling and emptying - no Kr-85 is set free and therefore for this sequence no krypton cleaning of the off-gas would be necessary.

For design purposes the following criteria can be assumed:

- heavy metal batch for one dissolution: 1000 kg
- krypton content for typical burn-up (40,000 MWd/t): 120 l Kr STP
- Kr-85 content: 8800 Ci Kr-85 (5 % Kr-85 after 7 a interim storage)
- time for Kr-85 liberation: 6 h
- time for full dissolving cycle: 12 h
- average off-gas flow: 100 m^3/h STP
- average Kr content in off-gas: .02 vol%
- cylinder size for interim of final Kr-85 storage: 50 l volume for 200,000 Ci Kr-85 (4)

A flow sheet for a full-scale krypton retention facility for the off-gas line of one dissolver is shown in Figure 6. It is assumed that NO_x and H_2O (and HTO) are separated continuously by batchwise operation of two molecular sieve units whereas only one krypton separation unit is necessary.

H_2O/NO_x Column Design

After off-gas precleaning the moisture amounts to 2.5 vol% H_2O and the NO_x concentration may vary between 0.04 vol% and o.3 vol%. Before separating the krypton from the dissolver off-gas, these NO_x and H_2O concentrations must be reduced to values below 1 ppm.

In order to minimize the adsorber volume required for H_2O/NO_x adsorption, the off-gas moisture is reduced to approx. 1 vol% by a condenser before entering the NO_x/H_2O adsorption columns. In this case the off-gas must be cooled to approx. 6°C.
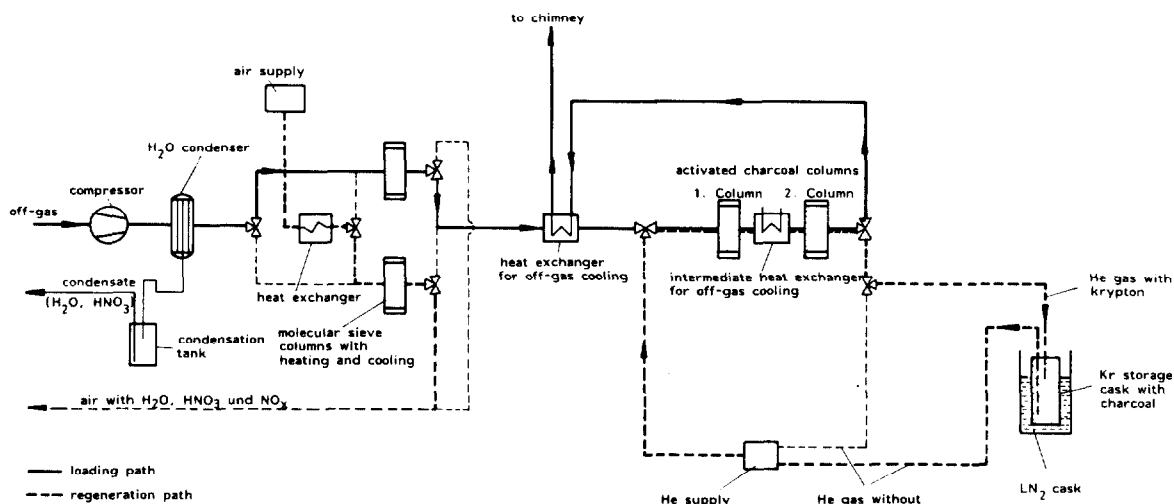
Figure 6: Flow sheet for full-scale NO_x, H_2O and Kr separation
for one dissolver off-gas line

Adsorptive H_2O/NO_x separation is carried out by 19 molecular sieve
columns connected in parallel with a height of 1400 mm and an inter-
nal diameter of 80 mm each. A heating/cooling medium (e.g. steam or
helium) is circulated around the columns for cooling and heating.
The basic design of the H_2O/NO_x adsorption column corresponds more
or less to the Kr adsorption column as shown in Fig. 7. One complete
unit is approx. 2 m in height and approx. 0.6 m in diameter.

Two such units are required for continuous NO_x/H_2O separation; they
are loaded and regenerated alternately in a 24-hour cycle, i.e. 12
hour for loading and 12 hour for regeneration.

Kr Column Design

The Kr separation from an off-gas flow of up to 50 m^3/h STP could be
carried out in a separation unit which is designed similar to the
design as shown in Fig. 4. But for even higher off-gas flows parallel
arrangements of such units would be necessary. This seems to be
too complicated. Therefore for high off-gas flows a parallel connec-
tion of columns as shown in Fig. 2 will be more practical. For
100 m^3/h STP dissolver off-gas some 99 columns with an activated
charcoal volume of altogether approx. 130 l are required. The
dimension of one column is 35 mm ID and 1350 mm length.

The design of the two adsorption units required for one process
section is identical and shown in Fig. 7. Helium is fed into the
units for cooling and heating, and flows around the activated char-
coal columns. So-called baffle plates are provided to improve a
regular heat transfer.

The Kr separation units are designed for a 6-hour loading phase
followed by 6 hours of regeneration so that continuous operation is
possible with 4 units whereas 2 units are connected in series.
Fig. 8 shows a diagram for the process sequence of the Kr separa-
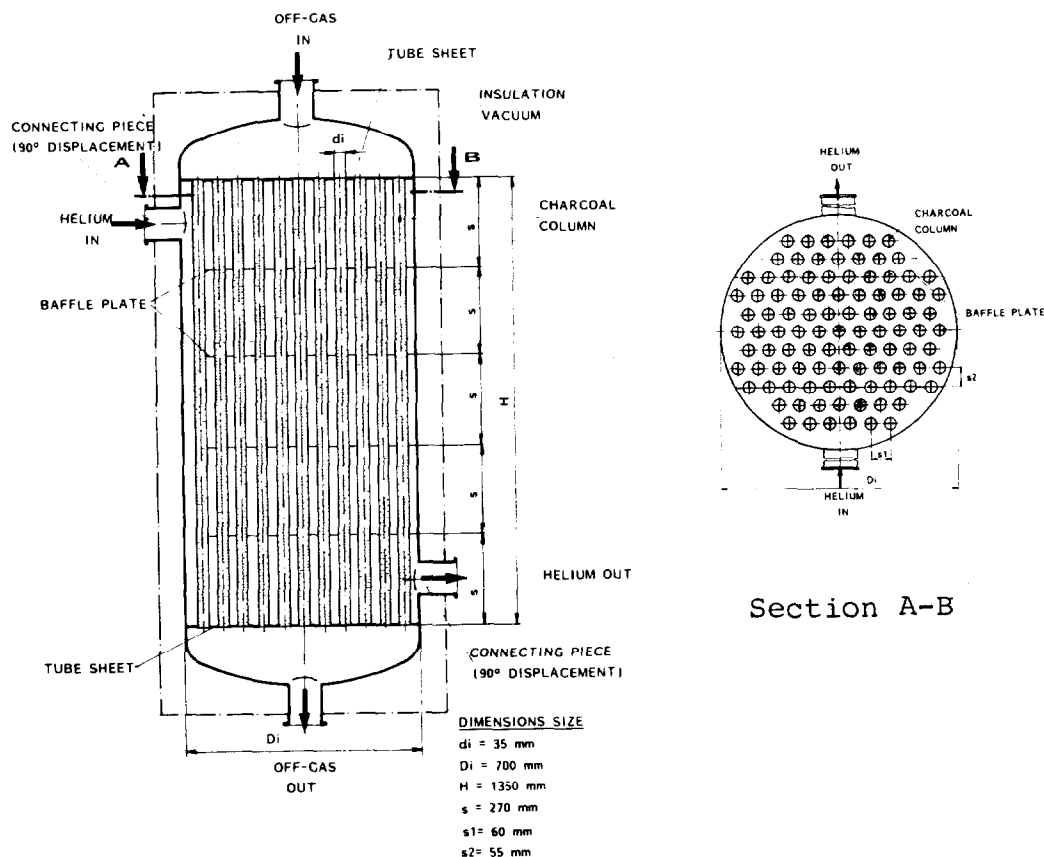tion plant. The heating and cooling times selected were checked by

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OFF-GAS
IN

TUBE SHEET

INSULATION
VACUUM

CONNECTING PIECE
(90° DISPLACEMENT)
A

di

B

HELIUM
IN

CHARCOAL
COLUMN

BAFFLE PLATE

HELIUM OUT

TUBE SHEET

CONNECTING PIECE
(90° DISPLACEMENT)

Di

OFF-GAS
OUT

DIMENSIONS SIZE
di = 35 mm
Di = 700 mm
H = 1350 mm
s = 270 mm
s1= 60 mm
s2= 55 mm

HELIUM
OUT

CHARCOAL
COLUMN

BAFFLE PLATE

s2

Ls1

Di

HELIUM
IN

Section A-B

Figure 7: Frontal section and cross section of the full-scale Kr
separation units
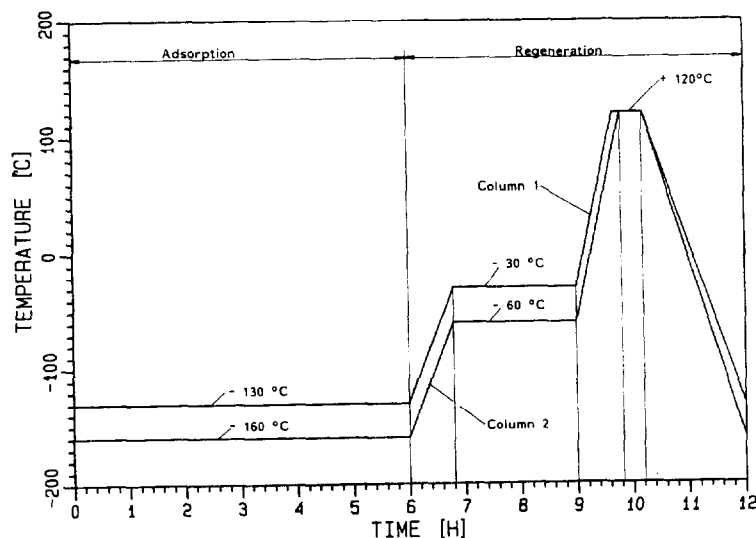
Figure 8: Diagram for process sequence for full-scale separation
plant for one dissolver off-gas line

thermal calculations and can be achieved with the selected helium heating/cooling system.

The total Kr-85 activity inventory in the separation columns amounts to approx. 8800 Ci after the 6-hour loading phase. During the column regeneration phase the Kr/He flow is fed into a storage cylinder filled with 50 l of activated charcoal and partly cooled by LN_2, so that the Kr is adsorbed again on activated charcoal. One 50 l storage cylinder is provided for the storage of 200,000 Ci of Kr-85 so that one storage cask is full after approx. 22 loading operations.

Acknowledgments

We would like to thank Mr. Frommelt and Mr. K. Hein for their experimental assistance.

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DISCUSSION

JUBIN: You indicated that you were unable to separate N_2 and Kr using a silver exchanged zeolite. Were you able to observe any separation between Xe and Kr using the silver zeolites?

RINGEL: We made no specific experiments concerning this question, but I am sure that Xe and Kr can be separated using silver exchanged zeolite.

GRUNDLER: How much are the costs for a large scale Kr^{85} separation facility?

RINGEL: We made no cost calculation.

HUTTER: We made no cost estimates, but there are cost values from AZUR planning for the WAK reprocessing plant at KfK. Also, the Japan Token Mura reprocessing plant has a cryogenic, retention facility ready to work with Kr^{85}

CONTAINMENT OF KRYPTON-85 BY AN ION-IMPLANTATION/
SPUTTERING PROCESS USING RARE EARTH ALLOYS

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Abstract

The design of a remotely operable ion-implantation/sputtering process for containment of krypton-85 in a solid metal alloy matrix is described. The process operates at subatmospheric pressure and is compatible with plants for reprocessing irradiated nuclear fuel that range in size up to 2000 metric tons of heavy metal per year. Process capacity is determined by the size, operating power and number of individual krypton-trapping storage devices (KTSDs) that can be operated simultaneously in parallel.

A 65-kW capacity nonradioactive multiple storage device unit was constructed using three unshielded test modules. The KTSDs contained composite targets with copper-yttrium surface area ratios of 1 and 5 to provide the matrix for the krypton product. Two of the KTSDs, with substrate surface areas of 1500 and 1000 cm^2, were operated simultaneously for over 3 h on a common manifold without an auxiliary vacuum pump. The other, a 1000-cm^2 unit, was tested for 1 h.

Krypton was incorporated at rates of 1.5 liters (STP) per hour for the larger and 1.0 and 0.7 liters (STP) per hour for the smaller KTSDs, respectively. A higher yttrium content in one of the smaller KTSD's target was responsible for the greater trapping rate in the smaller units. The energy consumption was 16 kWh per liter for the 1500-cm^2 substrate KTSD and was 20 and 26 kWh per liter for the two smaller units; the unit with the higher energy consumption had the lower yttrium content target.

Radioactive tests, using a total of 382 curies of a krypton mixture containing 4.2% krypton-85, were performed to verify that the β particle flux did not adversely affect the process and to provide representative krypton-85 storage product for long-term elevated-temperature testing. Three bench-scale KTSDs, with a substrate area of 345 cm^2 and containing 80 to 150 curies each of krypton-85 implanted in a copper-yttrium alloy, are being stored at temperatures ranging from 150 to 350°C. Periodic sampling is in progress.

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* Operated for the U. S. Department of Energy by Battelle Memorial Institute.

I. Introduction

Current U.S. regulations limit the release of krypton-85 to 50,000 Ci/10^9 watt years of electrical energy, or about 15% of the total krypton-85 produced in light water reactor (LWR) fuels.[1] To meet these requirements, storage in pressurized cylinders is the only available method.[2,3] To improve safety and increase economy, the Department of Energy chose to develop and evaluate other concepts for krypton immobilization.

Pacific Northwest Laboratory (PNL) has completed a program to develop ion implantation of krypton in a rapidly growing sputter-deposited metal as the primary method for producing the ultimate waste form for the storage of radioactive krypton. Bench-scale work begun in July of 1976 indicated that this process was well suited for producing thermally stable solids containing an excess of 5 at.% krypton.[4] It was shown experimentally that the highest krypton concentrations and lowest energy requirements were obtained by implanting the krypton in amorphous alloys.[5] A recent report summarizes the selection of alloys for this process.[6]

A study comprising preconceptual engineering design, technical evaluation, and life-cycle costing data was completed for comparing ion implantation/sputtering and zeolite encapsulation of krypton-85.[7] The study results were presented, and a review panel appointed by the DOE Airborne Waste Management Program Office recommended that the ion implantation process be selected for pilot-plant implementation. The main advantages of the process are:

● It operates at subatmospheric pressure.

● It permits high krypton loading.

● It produces a waste form that is thermally stable and has high thermal conductivity.

The original objective of the krypton ion implantation program was to design, construct and demonstrate the operation of a full-scale remotely operable nonradioactive immobilization unit. Later this objective was modified to include design of a smaller KTSD suitable for use with a Breeder Reprocessing Engineering Test (BRET)-scale reprocessing pilot plant (~15 MTHM/yr.) Construction was limited to fabricating three unshielded KTSDs connected to a common manifold to demonstrate process operations. A final task was added to carry out three multicurie laboratory-scale krypton-85 implantation experiments to provide small KTSDs for long-term thermal release tests for a copper-yttrium-krypton matrix.

The work reported here covers three topics:

● design of a remotely operated krypton immobilization station compatible with two sizes of KTSDs

- operation of a multiple-module unshielded nonradioactive krypton immobilization station with a one liter per hour trapping rate

- the results of three fully radioactive bench-scale test runs, in which a total of 382 curies of a 4.2% krypton-85 mixture were immobilized.

The operating principle and design concepts are described in Section II. The design of the remotely operable station is found in Section III. The unshielded multiple-module station and the results of its operation are discussed in Sections IV and V. The radioactive bench-scale tests and provisions for long-term elevated-temperature storage tests are described in Sections VI and VII.

II. Operating Principles and Design Concept

Because krypton does not form stable compounds with other elements, successful isolation of large quantities of krypton-85 in a stable solid requires an efficient process that "glues" the krypton atoms to a surface long enough to cover them with other atoms.

Trapping gases in metals exposed to a gas discharge is almost as old as sputtering.[8] Commercially manufactured ion pumps are widely used in industry for achieving an oil-free ultra-high vacuum. Unfortunately, these pumps are unsuited for immobilizing krypton-85 recovered from irradiated nuclear fuel because their design was optimized to pump active gases in a very low pressure regime ($<1 \times 10^{-3}$ Pa).

Krypton can be "glued" to a substrate by first ionizing it and then implanting it with the aid of an electric field. If the substrate is a growing film of suitable material, concentrations of krypton exceeding several atomic percent can be trapped in this solid matrix.[9] Resputtering and reemission of the krypton can be minimized if the implantation energy can be kept low. Since this form of "glue" requires ionized krypton atoms, it makes sense to use the krypton ions to sputter-deposit the matrix atoms also. This may be conveniently accomplished by placing the collecting surface (substrate) and the sputtering target (matrix atom source) in a concentric arrangement. Figure 1 provides a simplified depiction. A reasonable collection efficiency is obtained for the sputtered matrix atoms if the gap between them is not too large. The gap, however, must be at least several centimeters to produce the discharge. Concentric cylinders and hemishells or pipe caps make strong, convenient shapes for substrates.

The simplest way to produce krypton ions in the space between the substrate and the target is to establish a glow discharge in the annulus filled with krypton at a pressure of ~10 Pa by applying a minus 3 to 5 kV to one of the electrodes. Whitmell in the United Kingdom demonstrated a half-scale pilot plant for immobilizing krypton in sputtered copper.[10] The U.K. process works by alternately implanting krypton in the substrate (outer electrode) and sputtering metal from the target (inner electrode) to coat the implanted layer. Trapping
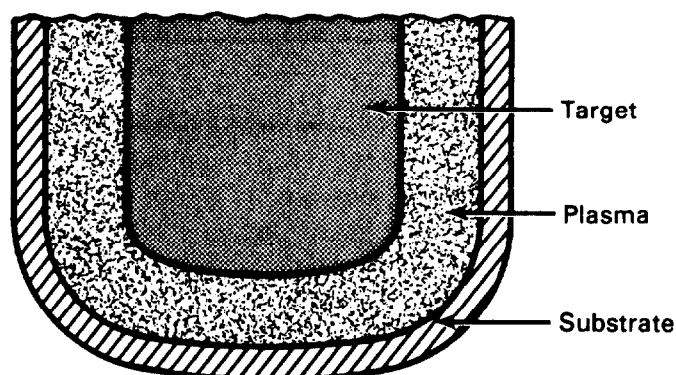
FIGURE 1. Concentric Arrangement of Collecting Surface and Sputtering Target

rate is controlled by a special thyratron switch controlling the relative times and voltages used for each phase.

A more efficient way to produce positive ions, and the scheme chosen by PNL, is with a low-voltage, thermionically supported discharge. This scheme has several advantages. First, the ion density can be controlled independently of the accelerating voltages placed on the target and the substrate. But more important, the ion density can be increased by a factor of ten or more over that obtained in the glow discharge. Also the presence of a "full"-time anode means the negative bias or ion-accelerating potential on the substrate is continuous, hence more efficient. The thermionically supported or so-called triode discharge is slightly more complicated by the need for additional electrodes (anode and filament) and their respective power supplies. This complexity makes it harder to build and easier to short out by film buildup or deposit flaking.

Regardless of the discharge scheme used, the object is to come up with an economical long-lived disposable trapping chamber with a high krypton trapping rate, capacity, and stable product. The filling process would involve the following steps: 1) evacuating of the chamber, 2) backfilling the chamber with inactive krypton and establishing the discharge, 3) ion etching the substrate, 4) establishing full-power pumping conditions, 5) switching to active krypton-85 and continuing to full capacity, and then 6) switching back to inactive krypton to apply a final closeout layer. For redundancy, ease of operation and flexible capacity, several small units should be operated in parallel rather than a single large unit. A krypton-85 immobilization plant would consist of one or more banks of the multiple-module KTSD stations. With appropriate biological shielding, it should be possible to maintain most of the equipment by direct contact.

Once filled, the KTSD would be disconnected and a protective pipe cap placed over the electrode flange and welded. After helium leak-testing, the unit would be stored for a time and then transported probably to a SURFF-type (spent unreprocessed fuel facility) dry well.[11]

III. Description of Full-Scale Remotely Operable Ion-Implantation/Sputtering Station

At PNL the objective was to develop a dual design which would immobilize the krypton-85 from a full-scale commercial fuel reprocessing plant (2000 metric tonnes of heavy metal per year) or a demonstration pilot plant (e.g., BRET) with a capacity of ~15 metric tonnes of heavy metal per year. The krypton is assumed to be 6% krypton-85 with an overall purity of 95%. To meet this range in capacity, two sizes of KTSDs were designed, with substrate areas of 3000 and 1000 cm^2. Each has a diameter of 30 cm and lengths of 30 and 10 cm, respectively.

Figure 2 is a cutaway drawing of the 1000-cm^2 substrate KTSD, a size which was built and used experimentally. Essential to the device is the centrally located water-cooled target made of copper or of a transition metal and filled with press-fitted plugs of yttrium, zirconium, or lanthanum. The composition of the alloy matrix is determined by the surface area and the sputtering yields of the two metals at the target-operating potential (~2400 V). The substrate surrounds the target concentrically. A single-turn tungsten filament, supported by six tantalum posts, and a cylindrical tantalum anode, located adjacent to the filament, serve as the auxiliary electron source and collector. The upper flange of the apparatus completes the vacuum envelope and supports the electrically insulated feed-throughs for the various electrodes. The upper flange and substrate, like the target, are water-cooled, while the other electrodes are uncooled. Allowing the anode and filament supports to run near the vaporization temperature for the matrix alloy minimizes the amount of sputter-deposited material available for shorting the closely spaced electrodes. The krypton gas is fed into the KTSD opposite the manifold port connection to give good control of pressure in the chamber. It is necessary to electrically isolate the krypton feed line from the substrate.

Figure 3 illustrates how the individual KTSD can be placed into a shielded carrier. The carrier can be moved laterally on rails to a location from which it can be raised in order to mate with the shielded service connector. In a single motion the KTSD is automatically connected to the pumping manifold, the krypton feed line, and all the necessary utility connections.

The critical parameters for scaling the size of the plant and providing the data for estimating the equipment, materials, and utility requirements are the KTSD pumping speed, energy consumption rate, and total krypton capacity. Formulas for calculating KTSD performance are given below. The estimated performance data for the 1000- and the 3000-cm^2 substrate KTSDs for $Ni_{.81}-La_{.09}-Kr_{.10}$ and $Cu_{.67}-Y_{.25}-Kr_{.08}$ are given in Table 1. It is assumed that each KTSD contains a uniform deposit 1 cm thick. The dimensions of the KTSDs, the sputtering parameters, and other pertinent data are found in the Appendix.
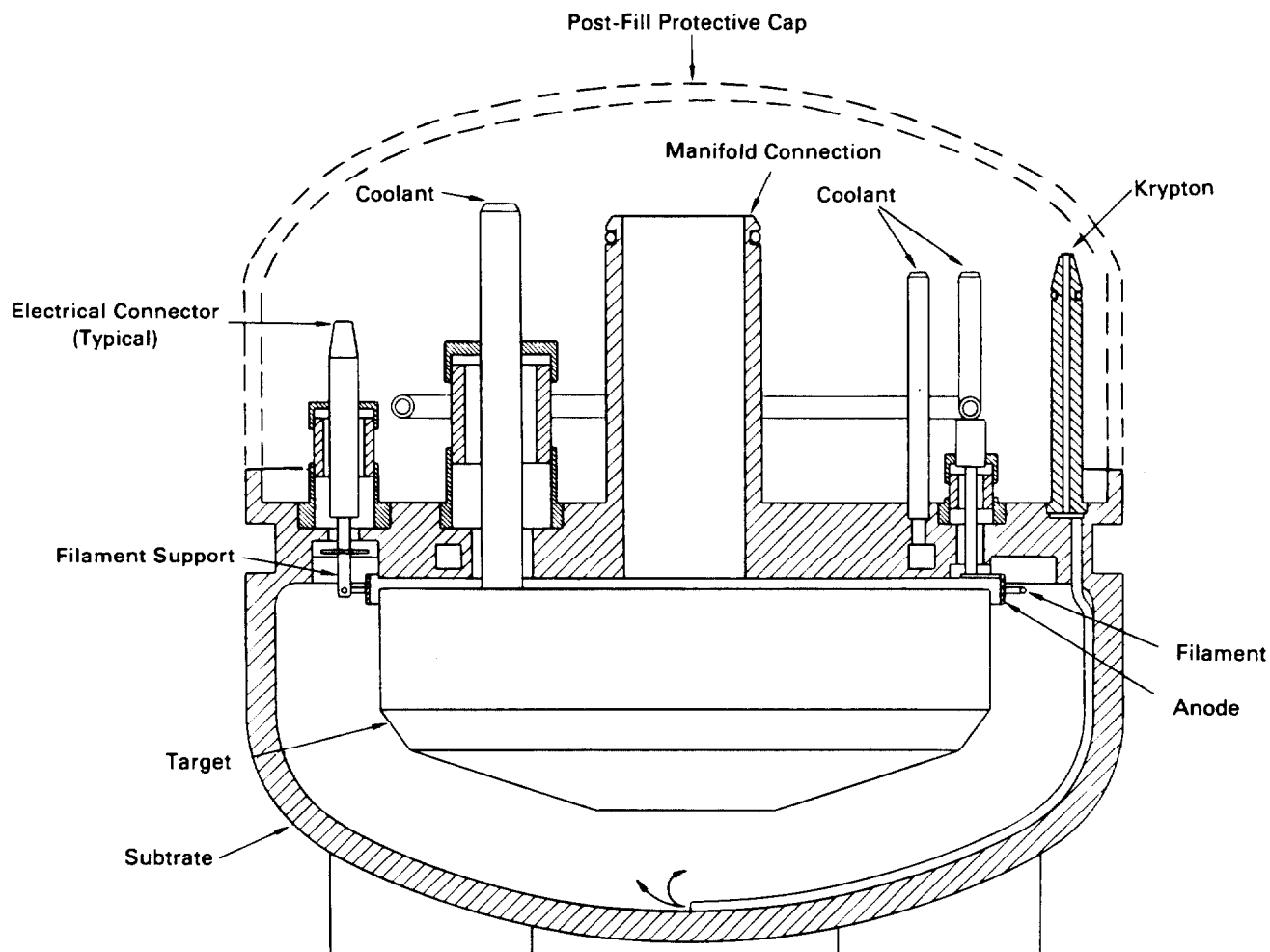
FIGURE 2. 1000-cm^2 Substrate Disposable KTSD

The trapping rate, S, of the KTSD is given by the following equation:

$$S = \frac{22.4 \; j_+ \; A_t \; Y \; C_{kr} K}{84} \quad (L/h) \; (at \; STP)$$

where: j_+ = positive ion current density
         A_t = area of the target
         Y = net sputtering yield (grams/A h)
         C_{kr} = weight percent of Kr trapped in the deposit
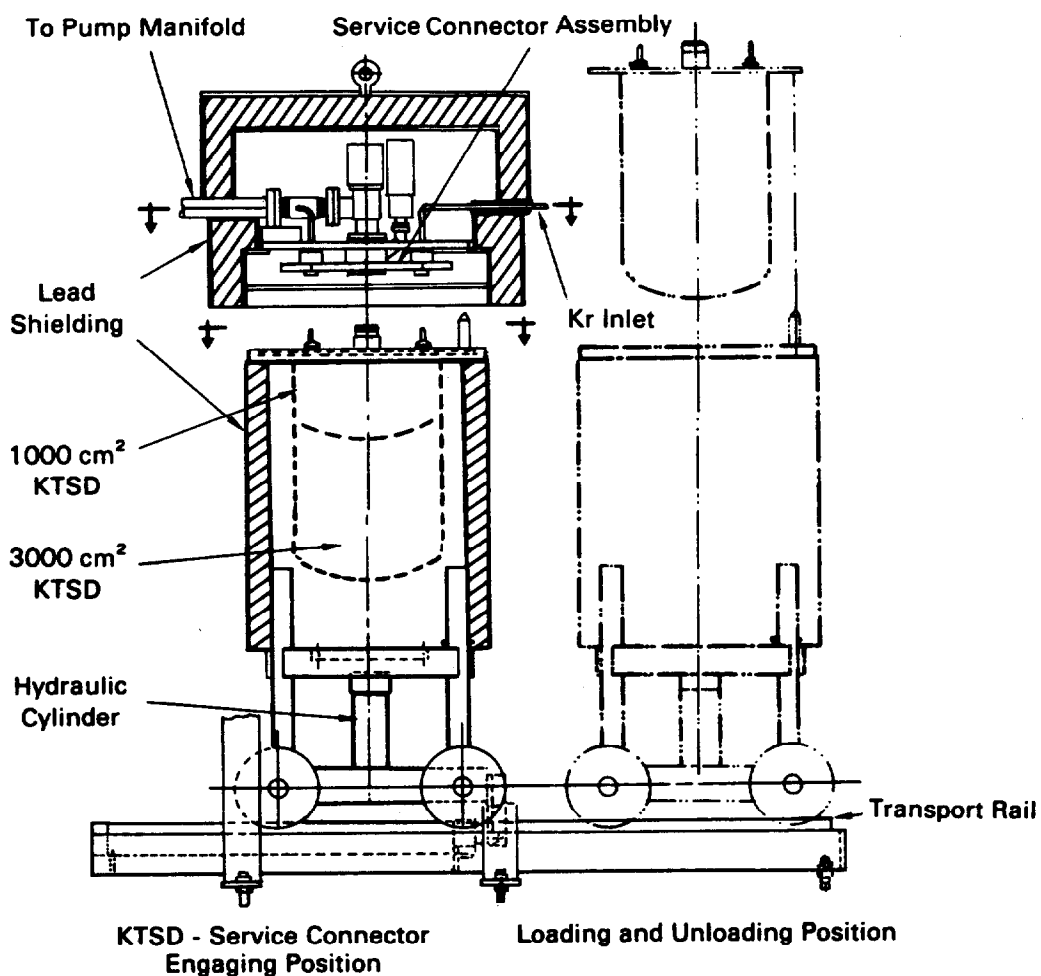 K = net fraction of the sputtered deposit collected by substrate.

FIGURE 3. Sputtering Station, Showing Shielded Carrier, KTSD, and Shielded Service Connector

TABLE 1. Estimated Performance Data for KTSD.

	$Ni_{.81}La_{.08}Kr_{.10}$		$Cu_{.67}Y_{.25}Kr_{.08}$	
Substrate Area, cm^2	1000	3000	1000	3000
Trapping Rate, S (L/h) (at STP)	1.4	5.4	1.0	3.9
Energy Consumption, E (kWh/L)	12	11	16	15
Storage Capacity, C (L)	199	616	117	414

The energy consumption, E, for the KTSD is given by the following equation:

$$E = \frac{V_t I_t + V_s I_s + V_p I_p + V_i I_i + V_f I_f}{S} \quad (kWh/L)$$

where: V_t, V_s, V_p, V_i and V_f are the voltages applied to the target, substrate, plasma, ignitor, and filament, respectively.

I_t, I_s, I_p, I_i, and I_f are the currents flowing through the target, substrate, plasma, ignitor, and filament, respectively.

The capacity for the KTSD is given by the following equation:

$$Capacity, \ C = \frac{22.4}{84} C_{kr} v_D \rho_D \quad (L) \ (at \ STP)$$

where: C_{kr} = weight percent of Kr trapped in the deposit
v_D = volume of the deposit
ρ_D = density of the deposit.

Using the results given in Table 1 for $Cu_{.67}-Y_{.25}-Kr_{.08}$ and the figures of 300 working days per year and operating three shifts per day with 70% equipment utilization, it can be shown that at least two banks of four KTSD modules each would be required to immobilize the estimated 210 m^3 at STP, or about 17 MCi of 6% krypton-85 released during the processing of 2000 metric tonnes of irradiated fuel per year.[12] (Figure 4 depicts a bank of four KTSD modules.) In contrast, only one 1000-cm^2 substrate KTSD would be required to immobilize the estimated 1.8 m^3 of Kr released during the processing of 15 metric tonnes of irradiated FFTF fuel per year (60,000 MWd/t cooled 180 days). The actual number of KTSDs cannot be determined for either size plant until a reliability factor is obtained by filling a meaningful number of units to full capacity, including the cap-welding and leak-testing steps.

IV. Description of Unshielded, Multiple-Module KTSD Station

It was considered very desirable to eliminate the need for continuous recirculation of untrapped krypton in the ion-implantation/sputtering process. This was primarily to avoid problems in maintenance of the krypton-85-contaminated pumps resulting from radiolytic decomposition of pump fluids and seals. Early prototype units with auxiliary pumps required recirculating up to 10% of the krypton feed stream. Three methods were considered for eliminating this necessity. The simplest was to find a way to operate the KTSD over a wider pressure range. The second method considered was the addition of a large ballast reservoir to the pump. And the third was to demonstrate that one or more KTSDs could be made to operate in parallel connected to a common manifold in close proximity without disruptive electrical interference.

Pump Manifold   Top View
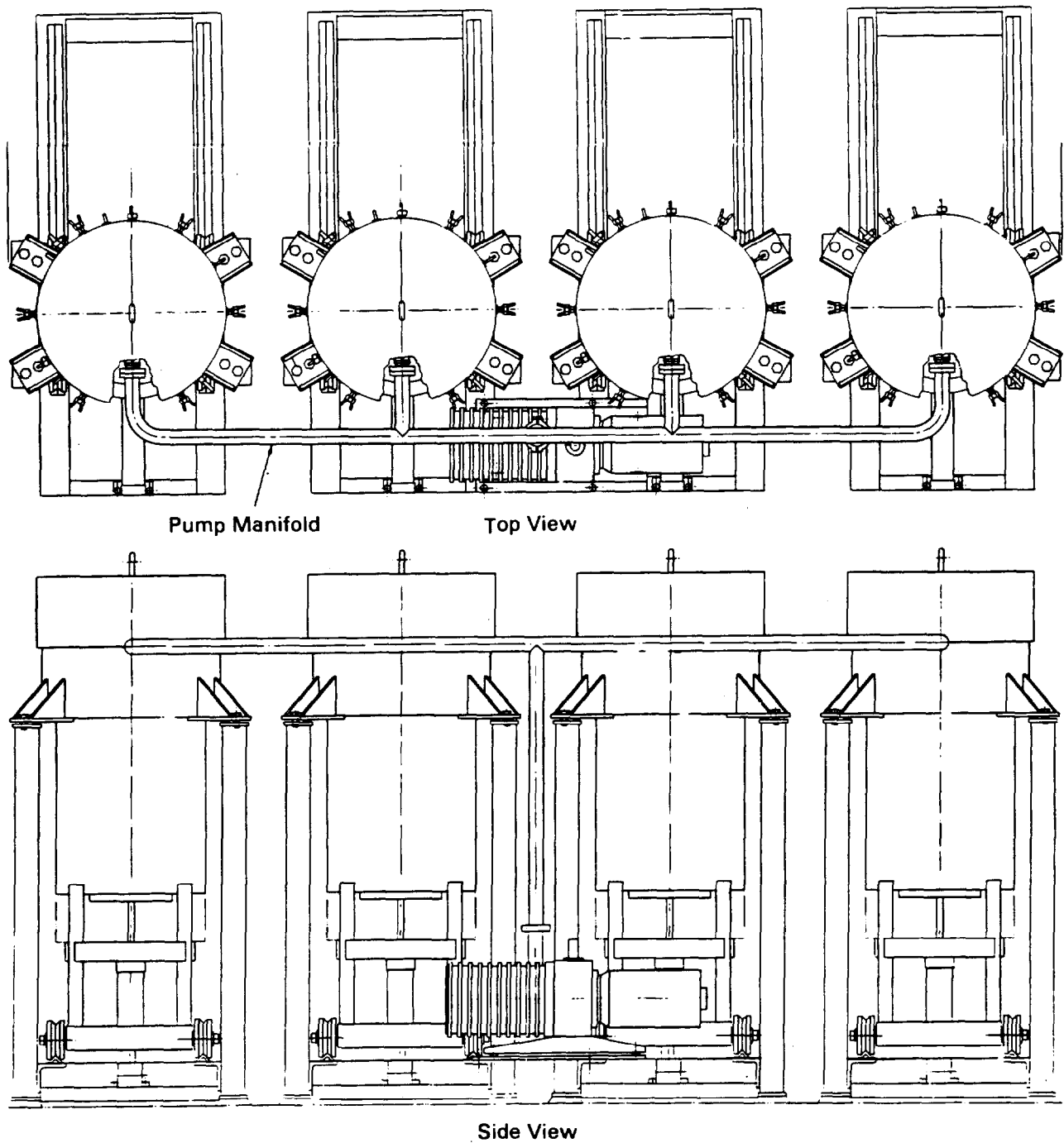
Side View

FIGURE 4. Bank of Four Remotely Operable KTSDs for a
Commercial-Scale Krypton-Immobilization Plant

It was discovered during preparation for the bench-scale radioactive experiments, discussed in Section VI, that the KTSDs could be made to operate over a much wider pressure range than previously thought.[13] Instead of 0.3 to 1 Pa they could, at least with the 345-cm^2 substrate unit, be made to operate over the range of 1 to 10 Pa. However, there was a penalty. When the pressure exceeded 1 Pa, the pumping speed decreased by more than a factor of 10. The frequency and magnitude of pressure bursts (caused usually by internal electrical arcs) which would raise the KTSD pressure above its most efficient trapping range would reduce the overall trapping speed. The addition of a ballast reservoir KTSD would handle most of the gas bursts observed in operating KTSDs with substrate areas up to 1500 cm^2. The ballast volume would require more space and shielding. For this reason the third method, use of multiple KTSDs in parallel on a common manifold, was chosen as the most practical for eliminating recirculation of krypton.

The main purposes for the multiple-module operation experiment were to:

- demonstrate the stable operation of a 1000-1500 cm^2 substrate area KTSD without the need of a continuously operating auxiliary pump

- demonstrate stable side-by-side KTSD operation

- evaluate the design of the 1000-cm^2 substrate area disposable KTSD using the copper-yttrium matrix alloy.

Three KTSDs were connected to a common manifold but insulated electrically by a short section of alumina tubing as shown in Figure 5. Each unit was equipped with its own fast-acting servo control valve for admitting krypton. This valve was located as close as possible to the KTSD and also insulated electrically by a short length of nonconductive tubing. The krypton feed rate was measured by individual mass flow meters. The power supplies and current interrupters are not shown, but a typical schematic wiring diagram is shown in Figure 6. The composite sputtering targets for each unit were fabricated from forged OFHC copper bar stock fitted with cast yttrium metal plugs pressed tightly into an evenly spaced array of holes.

Figure 7 is a cutaway view of Unit 1, a demountable version of the 1000-cm^2 substrate disposable KTSD (seen in Figure 2). A demountable version was chosen to simplify post-run examination as well as making any electrode modifications. The Cu-Y surface area ratio for the target was 1.0. Unit 2 was a 1500-cm^2 substrate pump with a target Cu-Y surface area ratio of 1.0. Unit 3 was a 1000-cm^2 substrate early-model pump with a Cu-Y surface ratio of 5. The internal electrode geometries of Units 2 and 3 were very similar to that of Unit 1. All three KTSDs used a one-turn, 50-mil (1.3 mm) diameter tungsten filament for the electron source. Units 1 and 3 were heated with 3-phase and 6-phase power, respectively, and Unit 2 was heated with dc.
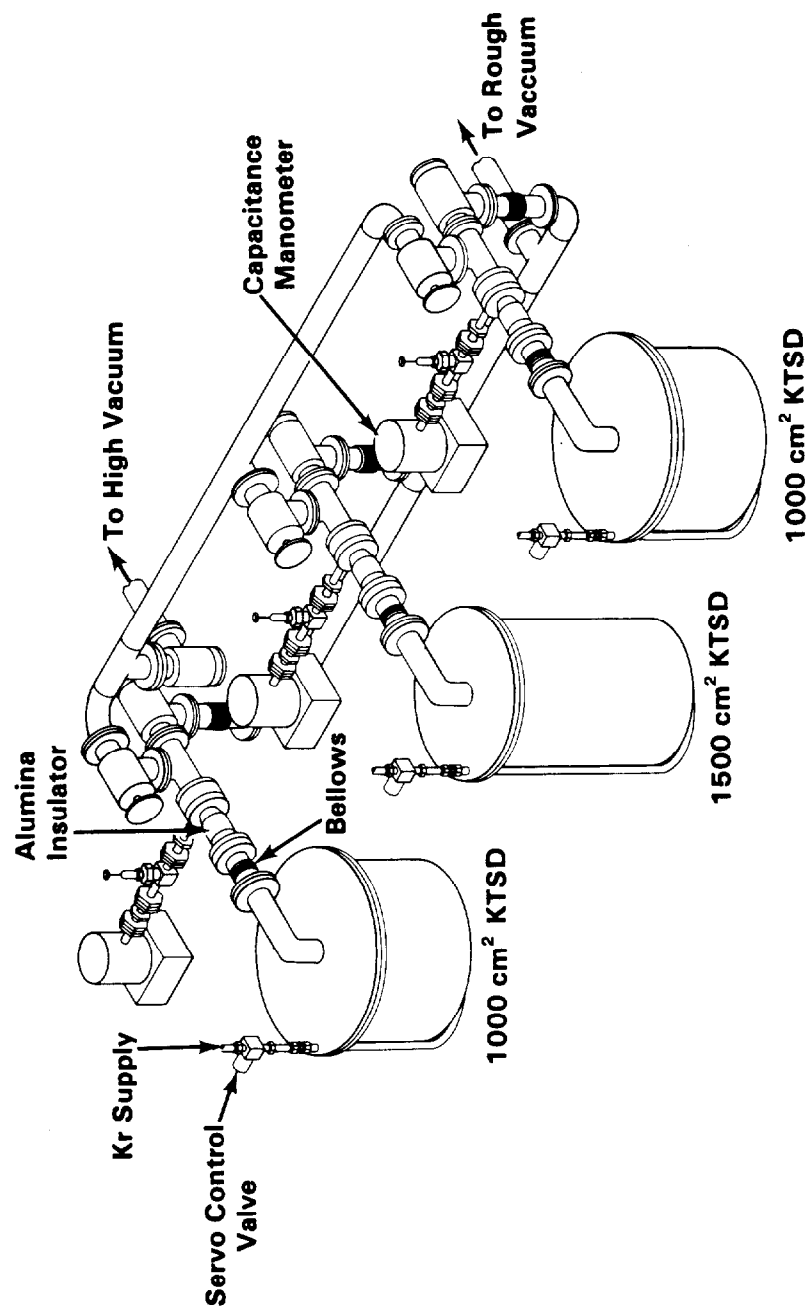
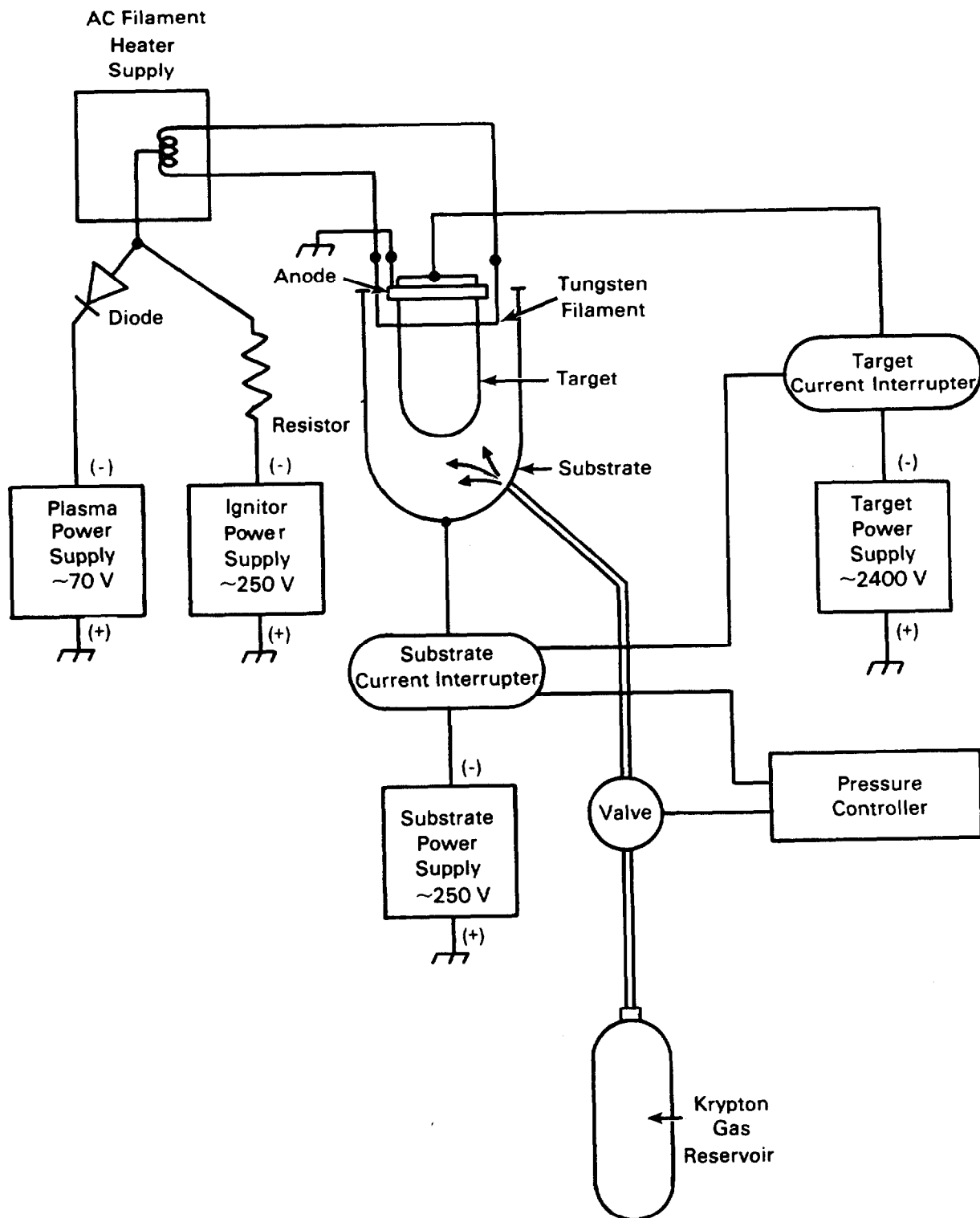FIGURE 5. Vacuum Piping Arrangement for Multiple-Module Krypton-Trapping Tests

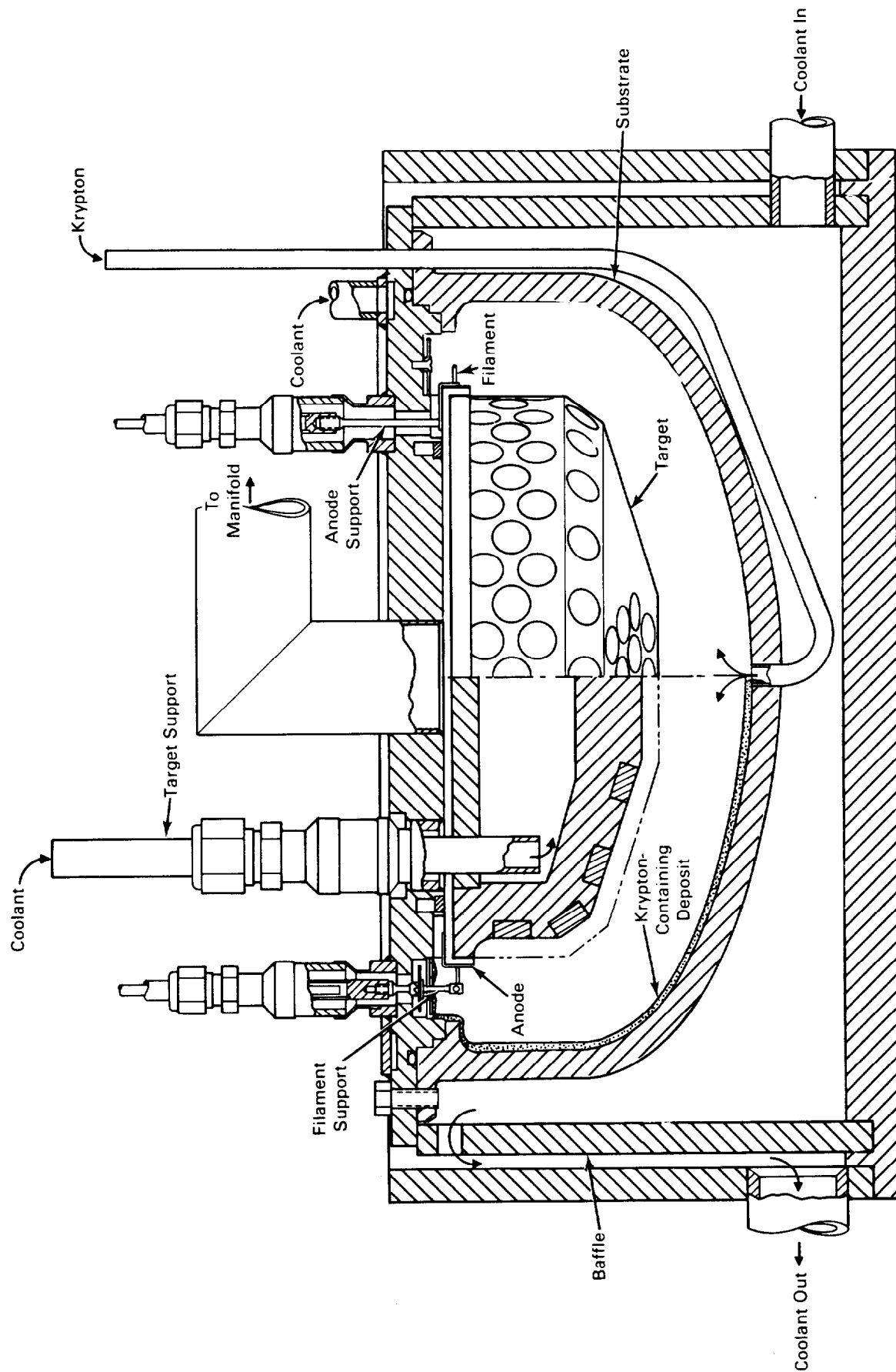FIGURE 6. Schematic Wiring Diagram for KTSD Operation

FIGURE 7. Unshielded, Demountable 1000-cm^2 Substrate KTSD

Lead shielding required for radioactive operation was not justified since only natural krypton was used. By eliminating the lead, some economy in fabrication was realized, but more important, the chance for electrical interference was increased. This produced a more rigorous test since the units were placed closer together and the lead was not there to act as an electrical ground shield.

V. Results and Discussion of the Multiple-Module Experiment

Before the multiple-module experiment was attempted, each unit was assembled and tested individually, first using an auxiliary pump and then closing the valve between the KTSD and the manifold. Typical operating parameters and pumping speeds are given in Table 2. All three units operated satisfactorily at their rated power when isolated from the auxiliary pump. Units 2 and 3 were restarted in sequence and run concurrently for a period of 3.5 h with no external pumping. While the units worked independently of one another, it was noted that pressure fluctuations during arcing were reduced.

Three conditions were found necessary to promote stable operation during arcing:

1. Both the target and substrate current interrupters must have "off" periods of less than ~10 ms.

2. Following an arc, the substrate current interrupter must signal the krypton feed control valve to close completely as rapidly as possible, and the krypton control valve must return to its original position just prior to the arc when the arc is extinguished.

3. In the case of an arc causing a loss of pressure control, normal operation is regained more rapidly if the substrate supply voltage is lowered to ~100 V, then raised slowly to the set point until the excess krypton has been trapped and the pressure is under control again.

The first condition was met by making a one-time adjustment in the timing circuits of the power supply current interrupters for Units 2 and 3. The power supply current interrupter timing circuits for Unit 1 were of a type that could not be adjusted to the required off period, so no attempt was made to operate this unit in the simultaneous mode. The second condition was met by modifying the circuits of a commercial pressure control unit. The third condition was met in this test by manually adjusting the substrate voltage, but control could easily be automated. The absence of disruptive electrical interference was fortuitous.

Three likely sources for electrical interference are the power supply current interrupters during cycling, poor grounding, and the nature of the triode discharge itself. There are three fast-acting current interrupters placed in series or built into the target, substrate and plasma power supplies

Table 2.   Operating Parameters Multiple-Module Experiment.

Unit	Substrate Area, cm^2	Target Area, cm^2	$\dfrac{\text{Area Cu}}{\text{Area Y}}$	Target V_t V*	I_t A*	Substrate V_s V	I_s A	Plasma V_p V	I_p A	Ignitor V_i V	I_i A	Filament V_f V	I_f A	Total Power, kW	Trapping Rate, L/h	Power Consumption, kWh/L
1	1000	547	1	2400	5.5	250	10	65	6	190	2	3	230	17	1.0	17
2	1500	981	1	2400	9	220	13.9	65	9.4	190	2	2.8	250	26	1.5	17
3	1000	547	5	2400	6.3	270	11	65	12.7	190	2	7.4	93	20	0.7	29

* V = volts; A = amps

for operating each KTSD. These interrupters serve to prevent damage to the individual power supplies and to the internal electrode structure of the KTSDs. The substrate power supply interrupter plays a special role in minimizing re-emission of krypton from the growing deposit caused by arcs or by KTSD control logic. These switches are capable of turning off up to tens of kilowatts of power in microseconds and hence could easily become powerful oscillators. Good grounding and low-inductance connections between the interrupters and the KTSDs, no doubt, were important in eliminating electrical noise. Under certain conditions, which are not well understood, noise in the kilohertz range, probably generated in the triode discharge, was observed superimposed on the dc supply voltages. This noise can cause the current interrupters to cycle unnecessarily, reducing momentarily the pumping capacity of the KTSD. This noise can be filtered by adding capacitance to the output circuits, but it is also important to minimize this capacitance to minimize the energy available for arcs.

VI.   Radioactive Bench-Scale Experiments

The 450 Ci of krypton-85 available was divided equally for loading three Cu-Y samples for long-term stability tests at 150, 250 and 350°C. Since the specific activity of the krypton-85 feed (4.2%) was representative of a commercial reprocessing plant stream, the experiments themselves were expected to reveal operational problems attributable to the high beta activity. Prior to the radioactive runs, a nonradioactive krypton implantation run was carried out to simulate conditions and to identify procedural problems and the need for additional radiation shielding. Later the loaded KTSD with nonradioactive krypton was used for accelerated thermal stability tests to identify the approximate temperature at which krypton would be released at a rate >1% in 10 years.

A 345-cm^2 substrate KTSD, with a composite target having a Cu-Y surface area ratio of 1.4, was surrounded with a minimum of 2.5 cm of lead shot, as seen in Figure 8. A schematic piping diagram, including the krypton reservoirs, pumps, KTSD, valves and miscellaneous sensors, is shown in Figure 9. This apparatus and its operation are fully described in Reference 13.
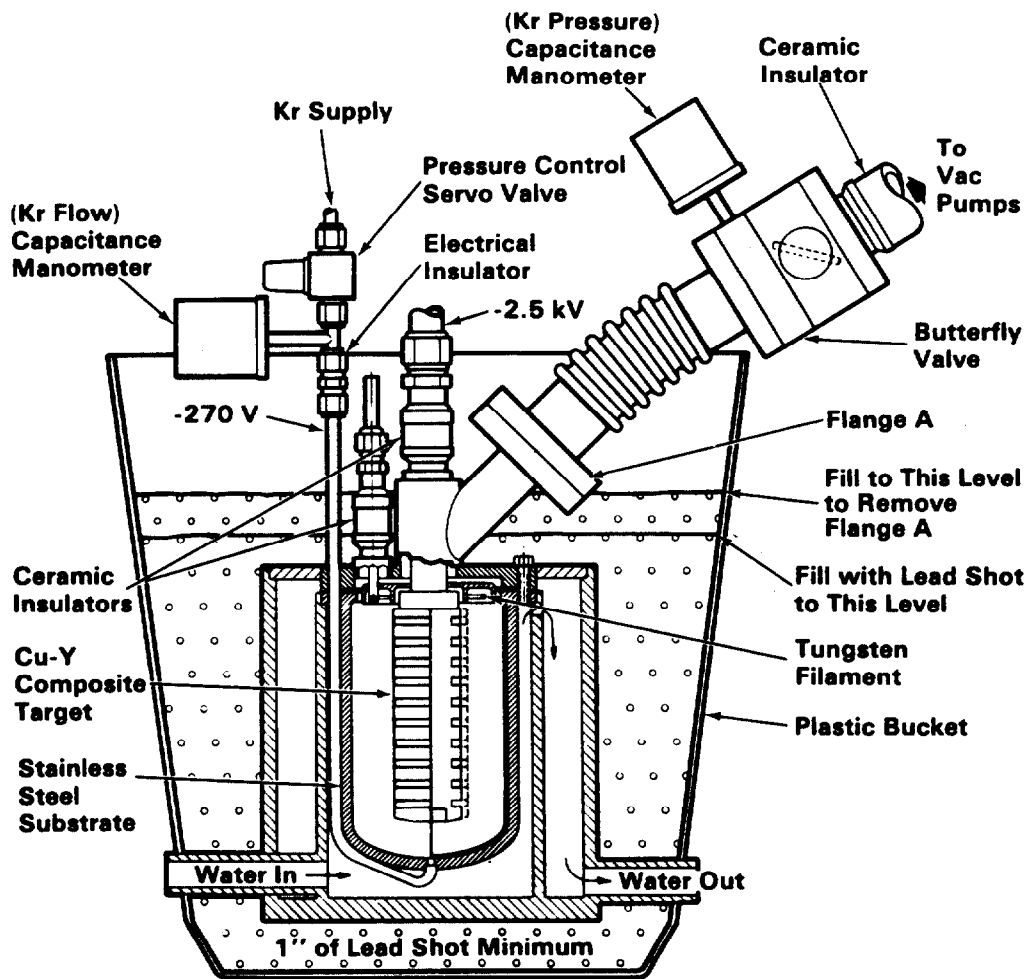
FIGURE 8. Multicurie Bench-Scale KTSD

One important feature of this KTSD apparatus was the exclusion of elastomer seals due to its intended use as a high-temperature storage vessel for up to 10 years. Viton and Teflon seals, however, were used extensively in other parts of the apparatus.

Briefly, the procedure for filling the KTSD was to evacuate and backfill with natural krypton. The substrate was then ion-etched before applying full power to the substrate and target. After ~1 h of operation the natural krypton supply was closed and krypton-85 of 98% purity was admitted. The major impurity was air, and the minor impurities were ~0.06% each of He, A, CO_2 and H_2. When all the krypton-85 was used up, the radioactive reservoir was closed and a closeout layer sputtering with natural krypton was added. The three layers were ~0.1, 0.5, and 0.04-0.1 mm thick in the order that they were deposited. A practice run was made with natural krypton, and a dummy reservoir
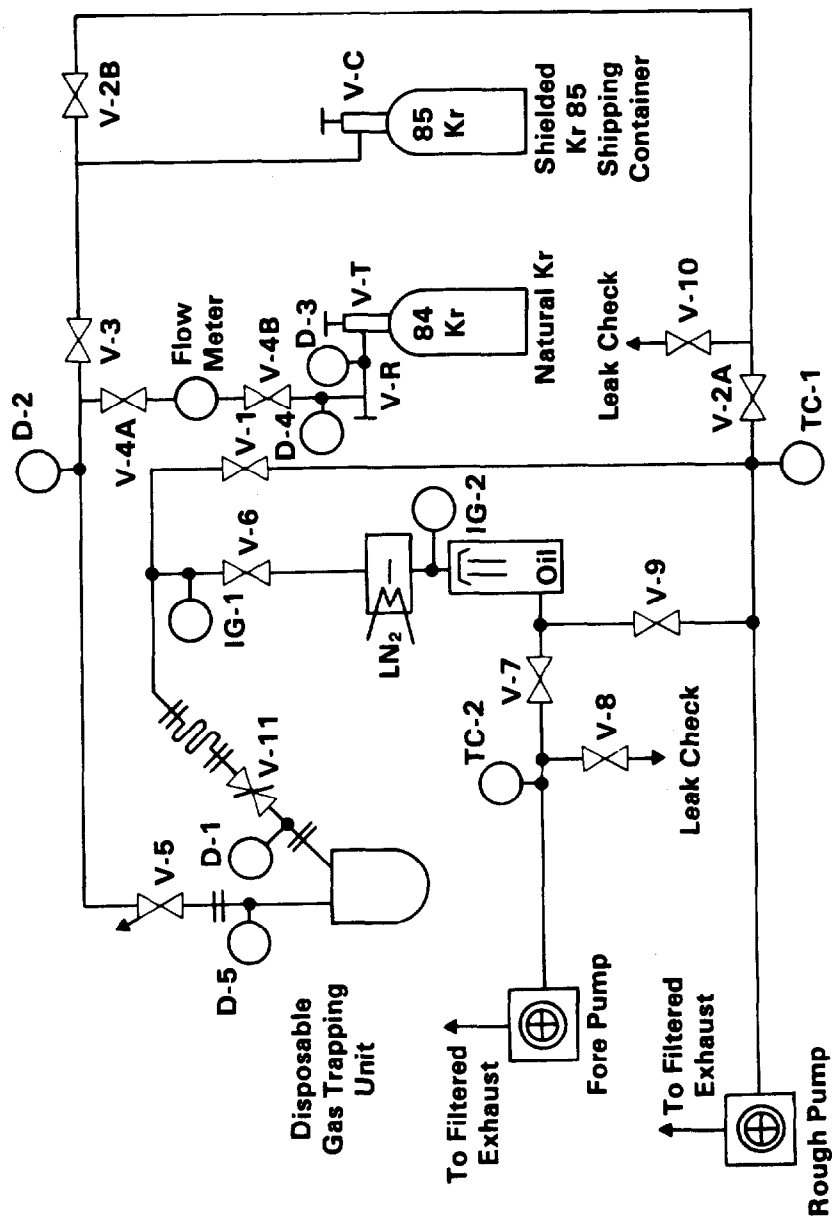
FIGURE 9. Schematic Piping Diagram for 150-Ci ^{85}Kr Bench-Scale Experiments

also was filled with natural krypton at ~0.5 atmosphere to simulate the procedure for the radioactive runs. The product from this run was saved for accelerated testing of thermal stability. Two radioactive runs were completed, immobilizing 150 Ci each. A target-to-anode short a little over halfway through the third run prevented trapping more than 82 curies in that deposit as well as adding the closeout layer.

The results from these runs showed no observable difference when radioactive instead of natural krypton was used. This is not surprising since the number of 40 eV electrons emitted by the filament is a factor 10^{12} times greater than the 0.7 MeV beta particles present in the space between the target and substrate apparatus at any one time. The small number of rubidium atoms produced in the space between the target and substrate would not be expected to cause any unusual effect either. Equally important, no radioactive particulate material was detected during disassembly of the KTSDs, even the third one without the benefit of the nonradioactive closeout layer. Each KTSD operated the entire radioactive portion of the run without the aid of auxiliary pumping, and thus allowed 100% recovery of the krypton. The trapping rate of the 345-cm^2 substrate KTSD could be varied from 0 to greater than 0.5 L/hr. The whole-body exposure received by the operator was low, ~25 mr/run.

VII. Long-Term Elevated-Temperature Storage Tests on Cu-Y-^{85}Kr

Long-term stability of the sputter-deposited krypton-metal matrix is important in evaluating the ion implantation/sputter-deposition process for immobilizing krypton-85 gas. Laboratory experiments using nonradioactive krypton trapped in a Ni-La sputter-deposited matrix have shown that krypton gas is released from the metal matrix at low rates by a diffusion process.[14] Gas release rates and the stability of the metal matrix may, however, be affected by the radiation field and transmutation products in an actual storage container of krypton-85. Consequently, experiments were started to measure the release of krypton-85 gas from multicurie-loaded Cu-Y-Kr deposits and to ascertain that the alloy is stable at elevated temperatures that bracket the anticipated long-term storage conditions.

Three multicurie Cu-Y-Kr deposits that are contained in the KTSDs are being used to determine the stability of the metal matrix during 5 to 10 years' storage at elevated temperatures. Temperatures of 150, 250, and 350°C were selected to bracket anticipated storage conditions. The three units are currently being stored at 150°C in lead-shielded casks, and the amount of krypton released from each unit will be measured after 3 months' storage. One unit will be returned to 150° while the temperature of the others will be increased in 100°C increments to reach their final storage temperatures, 250 and 350°C, respectively. Gas release will be measured at 3-month intervals during the initial heat-up periods and at 6-month intervals thereafter. One nonradioactive Cu-Y-Kr deposit prepared identically to the multicurie deposits will be subjected to accelerated thermal testing to provide an early warning of

any major release of krypton unrelated to radiation damage or growth of the rubidium daughter into the Cu-Y-Kr product.

A diagram of the storage cask configuration is shown in Figure 10. The cylindrical cask was fabricated from stainless steel sheet in a double-walled configuration. Lead shot was used to fill the 3.8-cm-thick wall cavity and, combined with a solid lead lid (3.8 cm thick), provides the necessary radiation shielding. Radiation levels were reduced from about 50 R/hr at contact with the KTSD to less than 25 mR/hr at the cask surface.
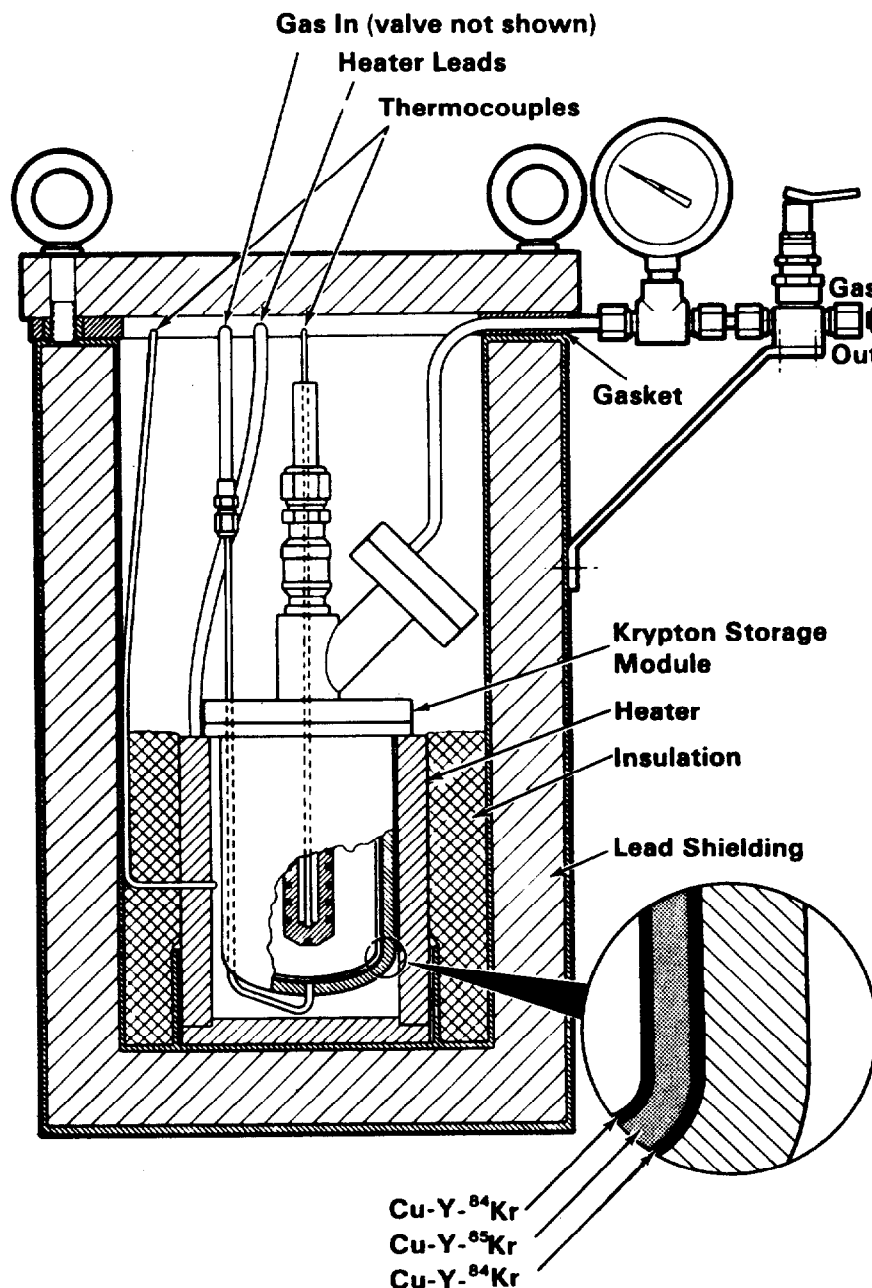
FIGURE 10. Bench-Scale KTSD Storage Cask and Heater

The KTSD is positioned within a clamshell heating element centered near the bottom of the cylindrical cask. Inlet and exhaust lines with valves outside the cask are provided for measuring release of krypton gas. The internal pressure of the unit is measured with a pressure gauge attached to the exhaust line. This gauge is monitored weekly and would provide early warning of an unexpectedly large krypton release from the metal matrix or of a leak in the containment. Thus, a significant increase or decrease in pressure would indicate a problem with the unit and the experiment would be terminated.

Temperature of the units is measured with chromel-alumel thermocouples and controlled with variable transformers. The temperature-power characteristics of each storage cask were experimentally determined by spot-welding thermo-couples directly to the side of a nonradioactive KTSD and measuring the wall and furnace temperatures as a function of power level. The data from these experiments were used to establish the proper furnace temperature and power level to obtain the desired KTSD wall temperature for long-term storage.

VIII. Summary and Conclusions

A preconceptual design was completed for a dual-scale pilot ion-implan-tation station for immobilizing krypton-85 in a growing sputter-deposited matrix. Plant capacity is determined by the number of units, size and matrix alloy selected for the individual krypton-trapping storage device (KTSD). The calculated capacity for a 1000- and 3000-cm^2 substrate KTSD loaded with a Cu-Y-Kr alloy 1 cm thick would contain the equivalent of 100 and 400 L of krypton at STP, or about 8,000 and 32,000 Ci of 6% krypton-85, respectively. The calculated trapping rate for the 1000-cm^2 KTSD operated at 17 kW would be 1.0 L/h. For the 3000-cm^2 KTSD the trapping rate would be 3.9 L/h operated at 58 kW total input power. An experimental reliability factor needs to be obtained before both the exact number of units for a given plant capacity and reliable cost figures can be determined.

After evacuation to <5 Pa, KTSDs of up to 1500 cm^2 substrate area will operate satisfactorily without the need of an auxiliary pump. Multiple KTSDs can be operated close to each other. Operating KTSDs on a common manifold improves the overall trapping efficiency of the combined units.

Tests using up to 150 Ci of 4.2% krypton-85 behaved similarly to identical nonradioactive krypton using a target with a Cu-Y surface ratio of 5. It was possible to disconnect the KTSD semiremotely once it was filled with 150 Ci of krypton-85, with minimal radiation exposure. No detectable radioactive particulate was found in the manifold piping.

Long-term tests in progress will yield information about the stability of the Cu-Y-Kr alloy and the construction materials used in fabricating the KTSDs.

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APPENDIX

Estimated Sputtering Parameters and Dimensions for KTSDs

Substrate Area, cm²	Target Area, cm²	Deposit Vol. (1 cm thick), cm³	V_t V*	I_t A*	V_s V	I_s A	V_p V	I_p V	V_i V	I_i A	V_f V	I_f A	Collection Efficiency (K), %
1000	547	765	2400	5.5	250	10	65	6	190	3	3	230	95
3000	2029	2685	2400	20	250	30	65	10	190	3	3.1	250	98

Properties of Matrix Alloys for KTSDs

Alloy	Net Sputtering Yield, Y, g/Ah	Estimated Density, ρ, g/cm	Krypton Concentration, C, wt. %
$Ni_{.81}La_{.09}Kr_{.10}$	7.9	6.8	12.7
$Cu_{.67}Y_{.25}Kr_{.08}$	7.6	6.2	9.4

* V = volts; A = amps

DISCUSSION

BASTIN: Will the planned long-term testing, if successful, qualify the packages for near-surface burial?

McCLANAHAN: Long-term testing of the three bench scale KTSDs will help qualify the copper-yttrium alloy as a suitable package, or waste form, for near-surface burial.

HUTTER: Can the presented Kr-85 sputtering system be connected to any Kr separation system directly without an intermediate buffer tank for Kr?

McCLANAHAN: Yes, the KTSDs described in this work can be connected to any separation system producing reasonably pure krypton with the help of a pressure reducing valve. You simply have to adjust the voltage on the power supplies to go from zero to full pumping capacity. I did not list that as a main advantage, but I don't see the need for a very large krypton reservoir if the head end of the process is large enough in the first place.

RINGEL: I have a question concerning the material loaded with Krypton-85. Isn't there a chance that this material may eventually become brittle with time and you will end up with a radioactive dust or aerosol problem?

McCLANAHAN: That's an excellent point. Of course, that is the purpose of long-term testing. The krypton-loaded rare earth alloys are all brittle but, as-deposited, form a monolithic solid. After each radioactive bench-scale experiment we checked the connecting piping for contamination with negative results. Whitmell, in the U.K., improved the mechanical and thermal stability of the krypton-containing metals he tested by raising the substrate temperature.

CROFF: Could you tell us what beneficial uses are being considered for krypton-85?

McCLANAHAN: Krypton-85 has been considered as a substitute for tritium for lights used in remote locations. Krypton-85 has also been considered as a low temperature heat source, e.g., oil pipelines.

CONDITIONING OF RADIOKRYPTON
USING ION SPUTTER PUMPS

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Abstract

Krypton ion implantation into sputtered metals seems to offer a safe conditioning and storage of fission product krypton separated in a spent fuel reprocessing plant. Various crystalline and amorphous metal matrices have been investigated in 1.0 kW laboratory scale ion sputter pumps. An amorphous Cu70/Zr30 alloy is favoured, due to its high efficiency and material properties.

Radial scale up of the laboratory pumps is simple. Longitudinal scale up was investigated in a dummy device by visible observation of the gas discharge. A relatively homogeneous discharge has been obtained for inner to outer cathode voltage ratios greater than four. One anode, which is front side earthed, is sufficient for such operating conditions.

The design of 10-15 kW pumps has been made in view of technical application. The total length is about 1.0 m with a sputter surface of 0.3 m^2.

Optimal operating conditions are sputter voltages of 2 to 3 kV and implantation voltages of 0.3 kV for Fe/Zr and 0.4 kV for Cu/Zr. Pumping rates between 2.0 to 4.0 L (STP) per square meter of sputter electrode surface have been reached. Effectivity has been as low as 13.0 kWh per 1 L (STP) of Kr. These results are in good agreement with previous laboratory data. Aspects for technical applications in a reprocessing plant are discussed.

I. Introduction

During the last 10 years an integrated system for treatment of the dissolver offgas was developed in the Institut fuer Heisse Chemie. This system, which exists in a semi-technical size, consists of three plate columns, which perform the nitric acid recovery and iodine desorption. In connection, a pressureless cold washing (Fig. 1) with freon 12 removes and separates the noble gases xenon and krypton.(1) Finally, the radioactive krypton is continously stored by ion sputter pumps preventing a high unconditioned inventory in the separation equipment and resulting in increased safety against leakage, as the system works without high pressure. This paper provides more details on the development of these pumps.(2,3,4,5)
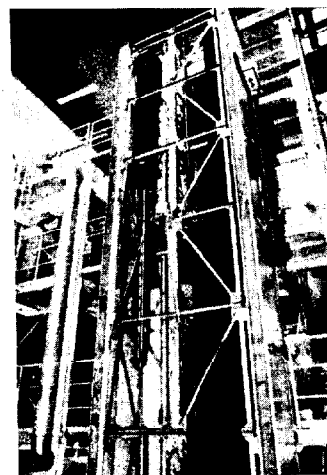
Fig.1 Noble gas scrubber

II. Experimental

1. The Experimental Pumps

In a first step some experimental pumps were constructed for fundamental testing.(6) Figure 2 gives the details of such a pump, which have an electric consumption of 1.0 kW. The inner cathode had a diameter of 40 mm and was fabricated of the testing sputter material. A voltage of -2500 V is applied to the this cathode to obtain a self-sustained krypton discharge in the annular gap, which has a distance of 30 mm, by a pressure of about one Pascal for sputtering the cathode material. The krypton is implanted by a voltage of -300 V to -1000 V into the continuously growing metal coating, which is collected on the inside of the outer cylinder. The upper and lower anodes are grounded. They are insulated against the cathodes by a gap of one millimeter preventing a discharge due to the Paschen Back law.
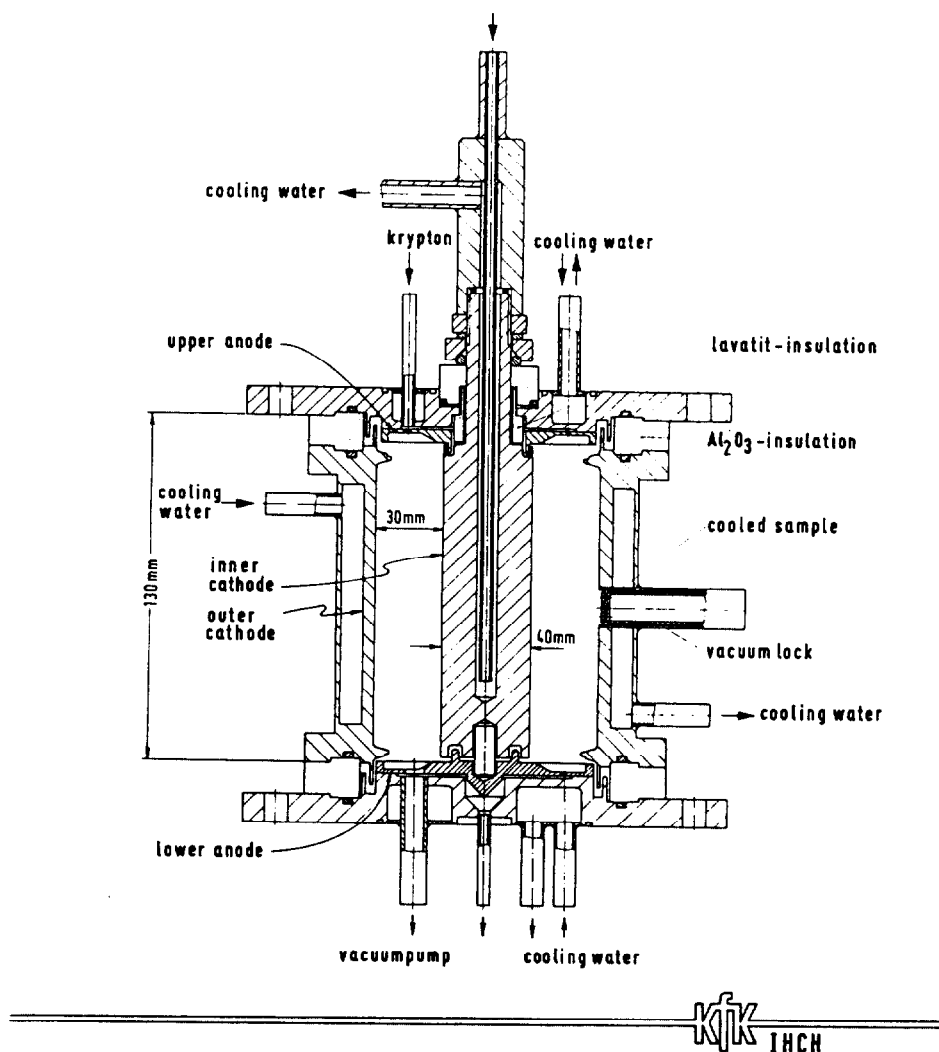
Fig.2   Design of the laboratory pump

2. Crystalline Material

First we used crystalline materials such as copper or titanium. These metals result in stable substrates with good thermal and mechanical properties. In Fig. 3 the left part gives a functional diagram of the pumping rate against the implantation and sputter voltage and the right part shows the power consumption. Here we find a minimum at 65 kWh/L(STP) Kr with an implantation voltage of -900 V and a sputter potential of -2.5 kV.

In Fig. 4 electron microscopic photos are shown of copper and titanium substrates containing up to 200 L(STP) Kr per liter metal in the upper row and the same material after a thermal treatment up to 1000 degrees C. Especially after heating the bubbles of krypton are more obvious.

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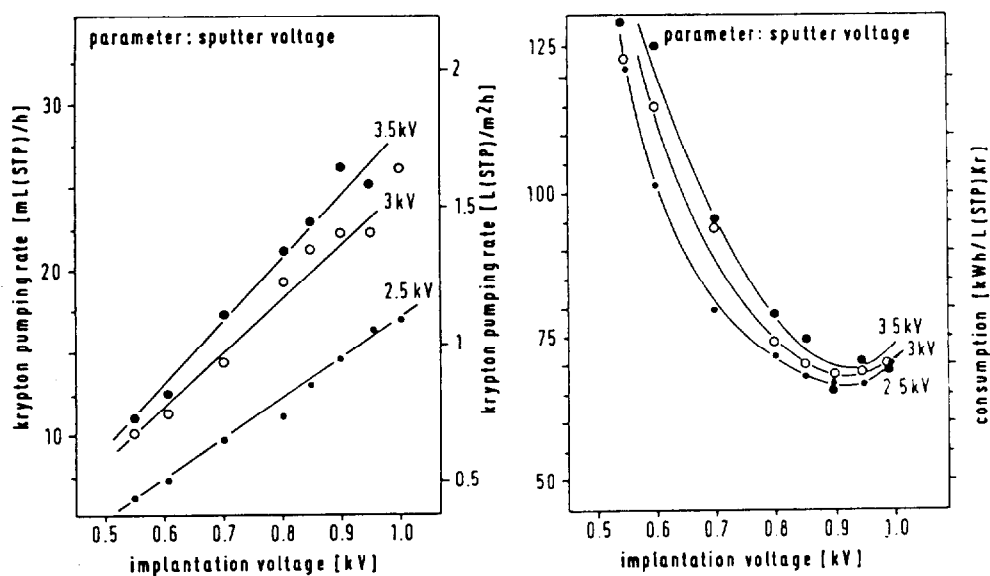
Fig. 3   Data of the Ti laboratory pump
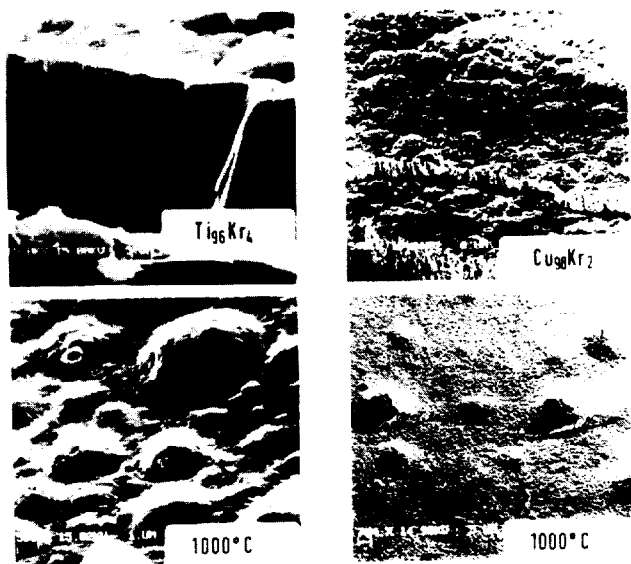
Fig. 4 Electron microscopic photos of
crystalline Kr-metals

3. Amorphous Material

By sputtering it is possible to produce amorphous alloys using two or more components with different atom diameter. Fig. 5 gives an example of a suitable element choice.
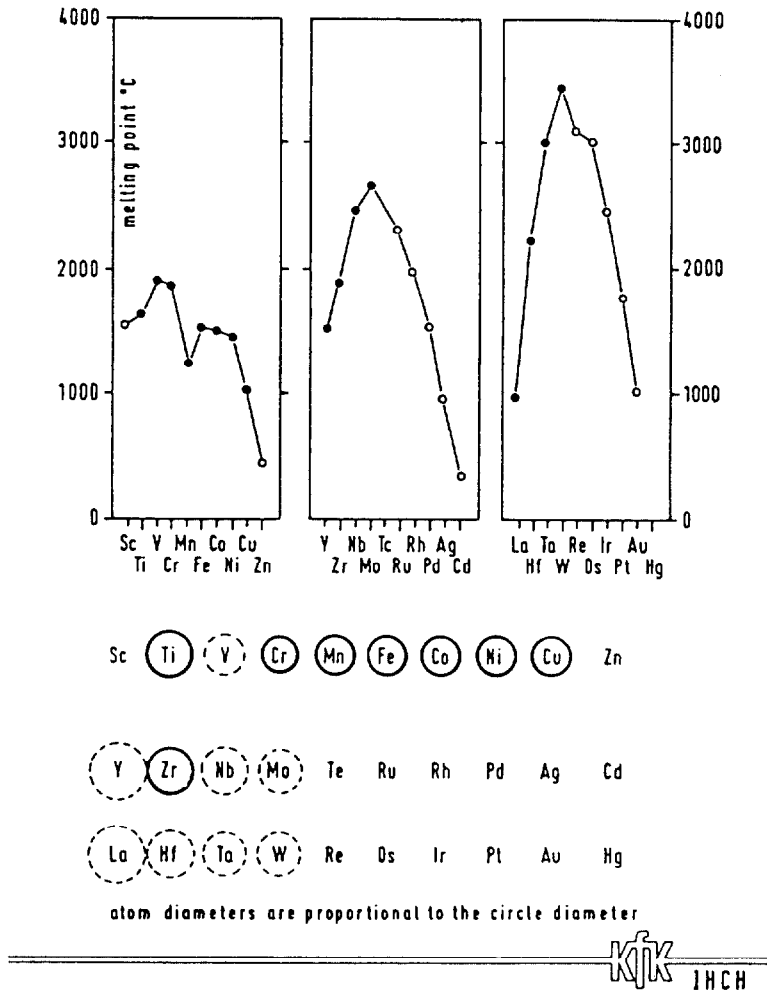
Fig. 5 Melting points of suitable metals

We selected Fe and Cu with 30% of Zr. Fig. 6 gives two examples for constructing such cathodes. One is fabricated by setting plugs of Zr into holes and the other by inserting strips of Zr into slots of the cathode. The amorphous deposits shown in the operation diagram (Fig. 7), emphasise the lower power consumption of 15 kWh/L(STP) Kr at the optimal implantation voltage of -350 V and a sputter potential of -2.5 kV.

The highest pumping rate was 4.0 l(STP) Kr/hm^2. Fig. 8 presents electron microscopic photos of such deposits before and after the annealing. Here the glassy edges show mussel-shaped fractures and demonstrate the amorphous structure which remains distinct up to 400 degrees C thermal annealing temperature. Above this definite temperature, which is a function of substrate composition, the deposit becomes porous in structure and the release rate of Kr increases. Neutron scattering and Mößbauer measurements suggested that the Kr atoms are distributed on single sites in the amorphous lattice.(7)
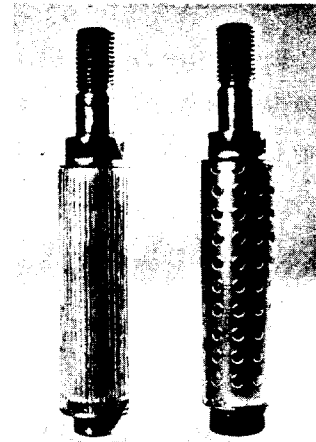
Fig. 6 Cathodes for sputtering amorphous Zr-alloys
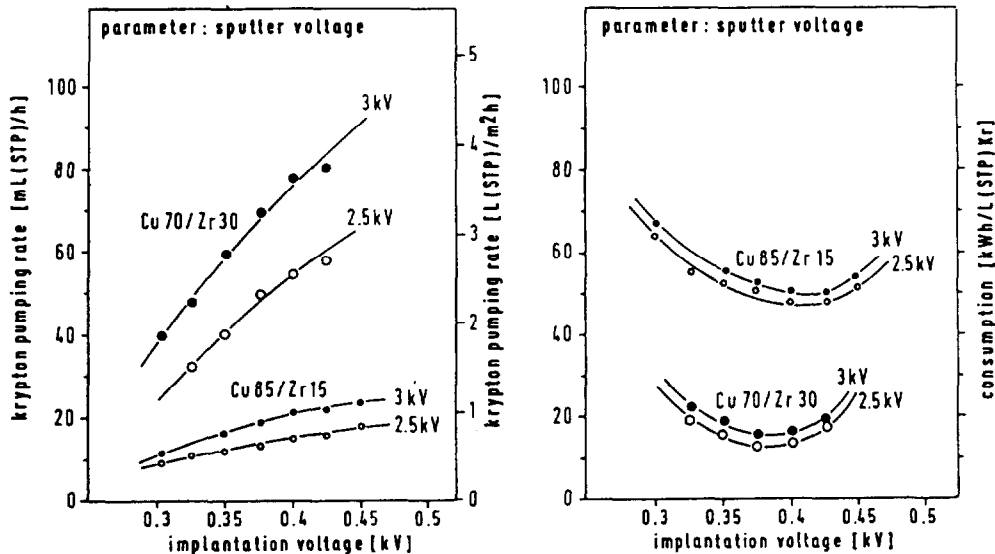
Fig. 7 Data of the Cu 85/Zr 15 and Cu 70/Zr 30 laboratory pump
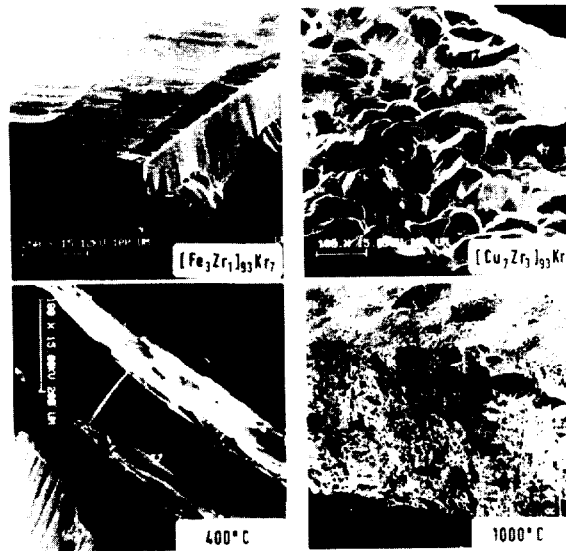
Fig. 8 Electron microscopic photos of
amorphous Kr-Zr-alloys

4. Summary of the Experiments

Fig. 9 gives an overview of the pumping rates and power con-
sumption of different material combinations as function of the
implantation and sputter voltage. The lowest consumption was reached
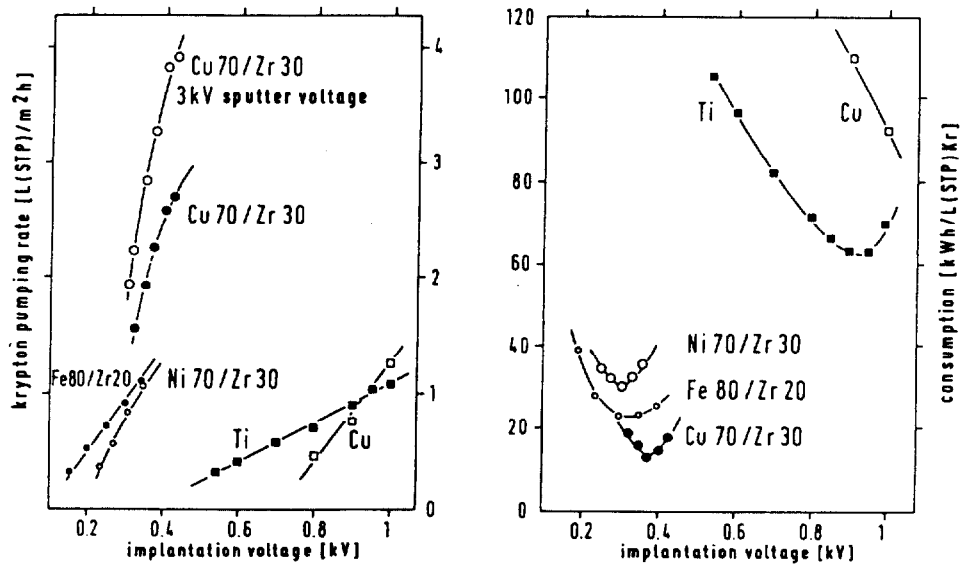with the Cu70/Zr30-alloy.

Fig.9 Pumping rates and power consumption of different materials
at 2.5 kV sputtering voltage

The comparision of the quasi steady Kr release rates given in % per year of crystalline and amorphous deposits in Fig. 10 shows, that these rates are in relation to the melting point of the used material. For the Cu-, Ti- and Cu70/Zr30-curves thin samples getting with the sample catcher were used. The Fe75/Zr25- and two Cu70/Zr30-measurements were performed with thick samples coming out of a spent pump. We suggested surface effects as reason for the big difference between the different Cu70/Zr30-results. These thermal release measurements show a very low release up to 400 degrees C. The total Kr amount released below this temperature up to steady state is less than 0.1 %.
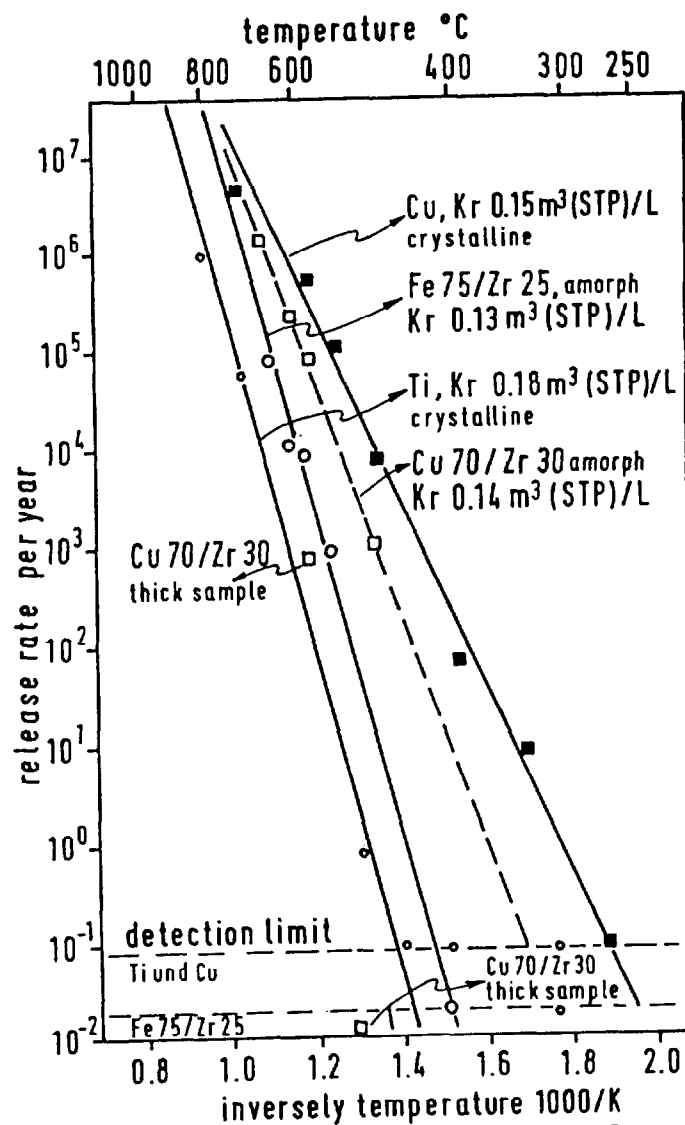

Fig. 10 Quasi steady Kr-release rates of different products

The following Fig. 11 shows a consumed Ti- and Cu70/Zr30-cathode. The different plasma density of the Ti-cathode during sputtering operation is in remarkable contrast to the uniform consumption of Cu/Zr-cathode due to its lower implantation voltage. Fig. 12 shows a sectional view of the Ti-pump after 700 h operation.
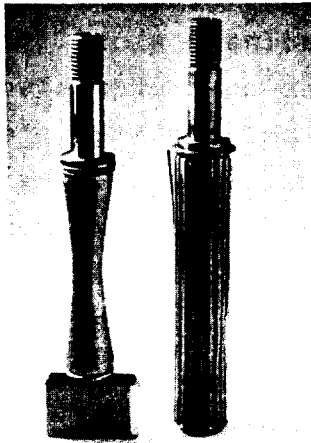

Fig. 11 Comparison of a spent
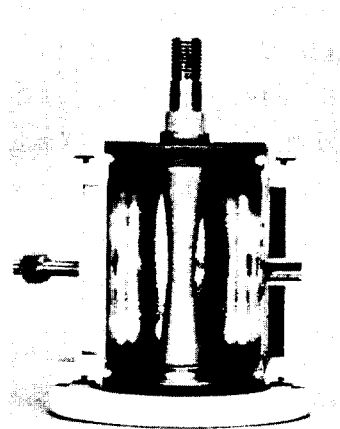   Ti- and Cu/Zr- cathode

Fig. 12 A sectional view of a
      spent Ti-lab. pump

III. Development of a Technical Pump

1. Fundamental plasma research

The scale up of the pump diameter seems to be without problems, but increasing the length is an unsymmetrical scale up. For plasma research, mainly by visible inspection, a glass tube with an identical electrode arrangement ebables rapid checking of the uniformity of the discharge under different potential conditions. We found only a uniform discharge with sputter to implantation potential ratios of greater than four. In this case no changes of the uniformity are detectable with only one grounded anode. Therefore, a lengthened pump with one anode works using amorphous material successfully only due to its low implantation voltage.

2. Construction of the Semi-technical Pump

A design of 10-15 kW pumps has been made in view of technical application. The total length is about 1.0 m with the outer diameter 0.18 m. This amounts to a sputter surface of 0.3 m^2. Fig. 13 gives an impression of the whole assembly. The cathode cylinder was made of thick Cu or Fe tubes with longitudinal slots containing Zr strips. The annular gap between the inner and outer electrode cylinders is about 3 cm. Gas, electric power and cooling water is supported only from the upper anode front side, where electrical insulation and vacuum tightness is provided by a 1.0 mm enamel layer. A cap welded to this side of the spent pump provides a second containment for Kr.
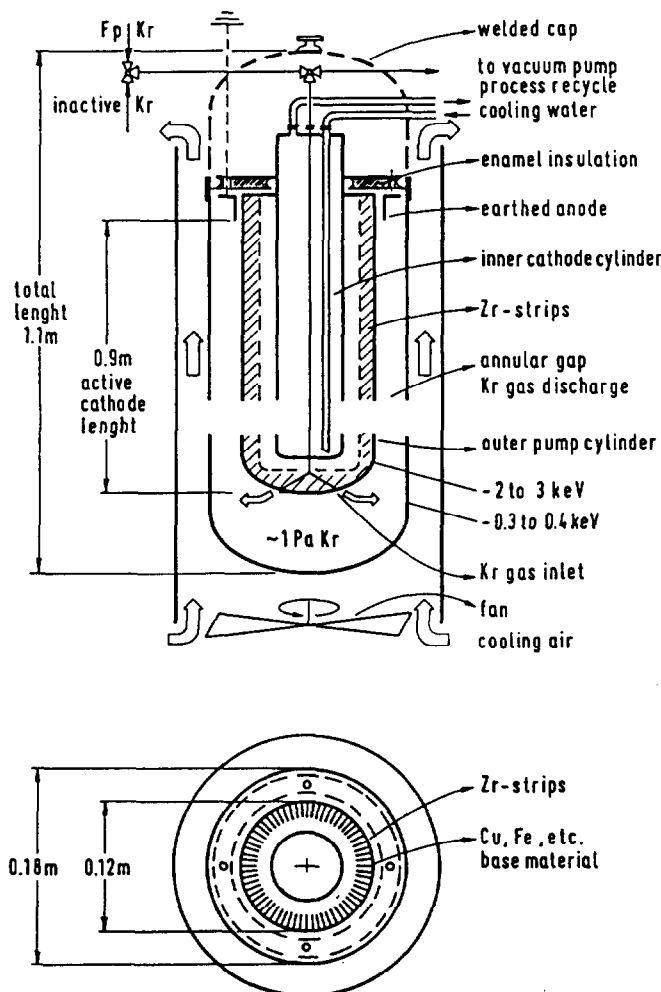
Fig.13 KR ION SPUTTER PUMP DESIGN PRINCIPLE

Matrix material peeling off in case of malfunction can be collected without disturbance at the lower spherical front side. The inner cathode cylinder is watercooled and the outer cylinder is aircooled by a fan to get better matrix properties at higher implantation temperatures of about 100 degrees C.

3. Pump Operation

The semi-technical pump is easier to operate due to its greater plasma volume. The electrode assembly must be fabricated very carefully because of the thin insulation gaps and the surfaces have to be smoothed.

At the beginning we used the Fe80/Zr20-cathode. The operation diagram, Fig. 14 is in good agreement with the data of laboratory pumps. Especially the pumping rates are remarkably higher.
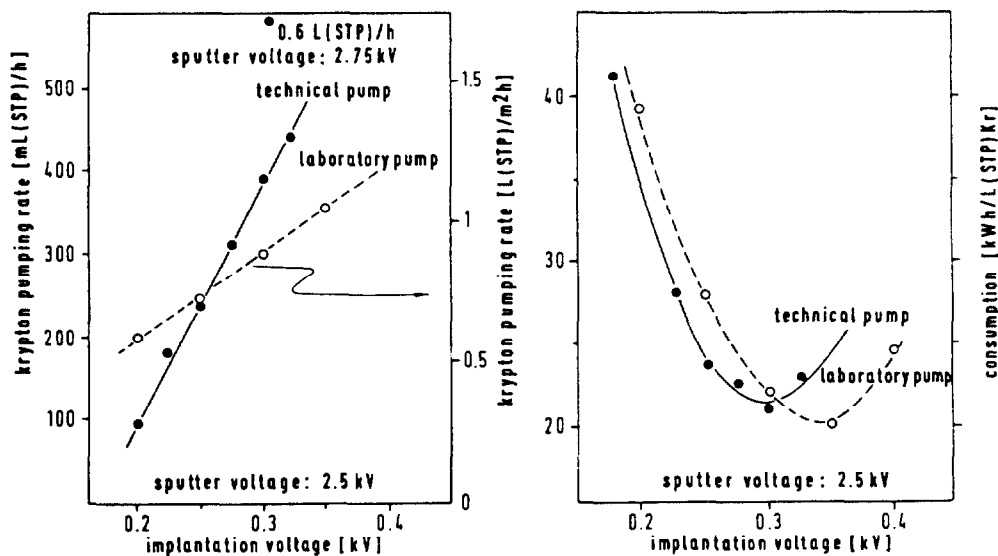

Fig.14   Data of the Fe 80 / Zr 20 technical pump

Fig. 15 gives the operation diagram of a Cu70/Zr30 cathode for a relative low sputtering voltage. We did not succeed until now to use higher sputter voltages and resulting in higher pumping rates because of extension cracks in the insulation enamel. These small crevices arose during the fabrication process. The pumping efficiency however corresponds very well to the laboratory scale pump.
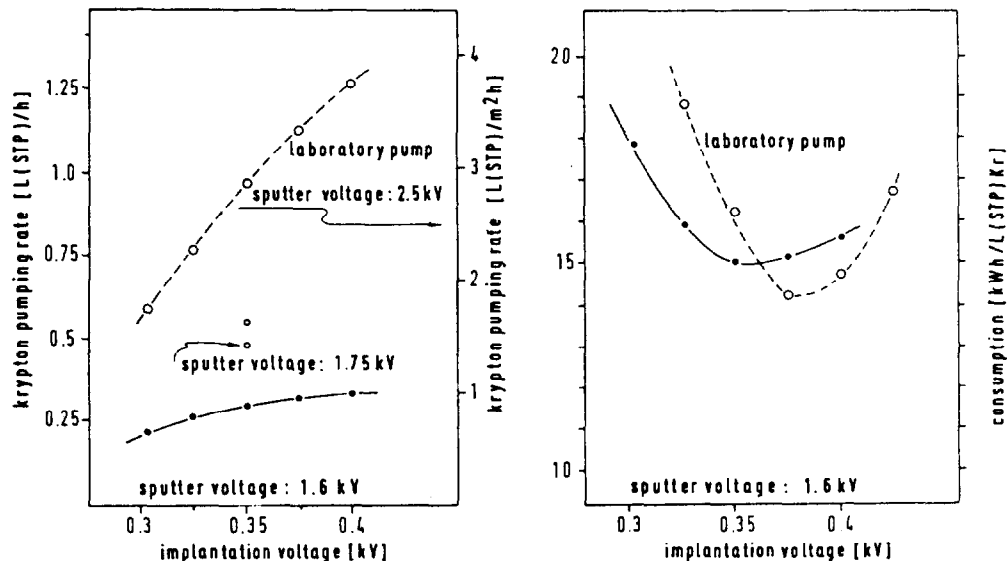

Fig.15 Preliminary Data of the Cu70/Zr30 technical pump

IV. Design of an Application

The practical application of such a sputter pump for a reprocessing plant is given schematically in the Fig. 16. The technical pump has a sputter cathode diameter of 0.3 m and a length of 1.2 m, which results in an active surface of 1.0 m^2 with a capacity of 3000 L (STP) of Kr. With a pumping rate of 4.0 L(STP)/h the daily rate of one pump is equivalent to dissolution of 700 kg spent fuel per day with a burnup of 30000 MWdt. During operation and handling the pumps stand in a moveable lead shielding. In a nonshielded cell
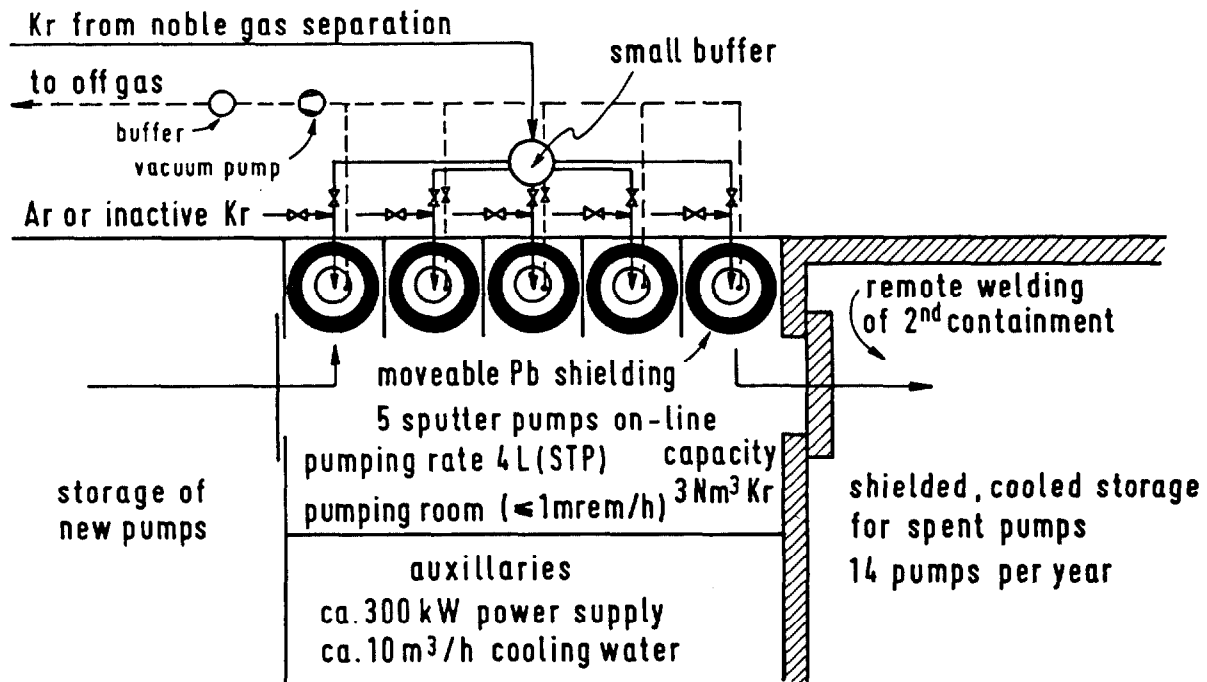
Kr from noble gas separation

to off gas

buffer

vacuum pump

small buffer

Ar or inactive Kr

remote welding
of 2nd containment

moveable Pb shielding
5 sputter pumps on-line
pumping rate 4L(STP) capacity
pumping room (≤1mrem/h) 3 Nm³ Kr

storage of
new pumps

shielded, cooled storage
for spent pumps
14 pumps per year

auxillaries
ca. 300 kW power supply
ca. 10 m³/h cooling water

KfK IHCH

Fig. 16 Design of a reference concept
(350 tons spent fuel per year)

with separate ventilation some of these pumps operate simulta-
neously. The total pumping rate is in accordance with the produced
Kr plus a reserve for changing a spent or a damaged pump. Small
buffers reduce the peak value during the dissolution of spent fuel.

The operation time for a pump is about one month. Damaged pumps
will be changed without overhaul. For changing the pump it is opera-
ted finally with inactive Kr for flushing the pipes and burying the
active Kr. After this operation, the gas, cooling water, and current
supply will be removed and the frontside will be closed by remote
welding of the end cup. Now the pump case is the second containment
for a safe storage.

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CLOSING COMMENTS OF SESSION CO-CHAIRMAN MOTES

The papers presented here have been concerned with the recovery and treatment of Kr-85. It is notable that this was the only radionuclide addressed, although papers concerning iodine and tritium will be given in Session 8. Work concerning krypton recovery is apparently reaching a relatively mature developmental stage. With work being largely focussed on final details and optimization, a continued decline in this work is to be expected. Ion implantation is also well along in development, with scale-up and optimization being considered, although testing of long-term waste form adequacy remains, and differences in the metal matrix composition are noteworthy. While some work remains to be done on krypton and iodine, and considerably more on tritium and carbon, the lack of an identifiable need results in very modest support and the likelihood that the required technologies would not be available if reprocessing were to move forward; in particular, the absence of generally accepted disposal technologies for each radionuclide. Attendant acceptance criteria uncertainties regarding allowable releases of tritium and carbon, and the lack of integrated recovery and treatment flowsheets, may well become limiting constraints.